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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on page 3 of the Journal cover. New tables will be announced from time to time as they become available.

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EVALUATING THE WEARING QUALITY OF CURRENCY PAPER

By Frederick T. Carson and Vernon Worthington

ABSTRACT

This report describes means which have been developed to determine the relative serviceability of currency-type papers. A reproducible crumpling and smoothing cycle has been developed with which to imitate the appearance and characteristics of worn paper currency. The changes in significant physical properties of this worn paper are then measured. An automatic, motor-driven crumpling apparatus is used, which alternately crumples and straightens out a specimen at a rate of about seven times per minute. The change in air permeability as the crumpling procedure progresses appears to be the most useful single measure thus far found of the decreasing serviceability of the paper. An air permeameter, specially designed for use in conjunction with the crumpling apparatus, is briefly described.

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I. INTRODUCTION

For several years the National Bureau of Standards has been engaged in research, supported by the Bureau of Engraving and Printing, to find means of increasing the useful life of the United States paper currency. Replacement of worn-out paper currency requires an annual expenditure of several million dollars. Any improvement leading to a longer average life, therefore, represents a substantial saving.

Changes made in composition, fabrication, and processing of experimental papers, in order to improve the serviceability of paper currency, have sometimes been appraised by the United States Treasury Department by means of actual service tests. Such tests are much too slow, however, for routine evaluations, and may be inconclusive, owing to the difficulty of getting enough returns on comparable treatments in service. A standardized laboratory test, capable of simulating in a comparatively short time the type of wear

which paper currency undergoes in circulation, is essential in this effort to further improve the serviceability of currency paper.

Wear of paper currency differs from wear in its more common connotation, inasmuch as abrasion, loss of substance, and breaking are not common causes of failure. Repeated folding and crumpling, and the incident soiling and defacing, are the primary factors responsible for withdrawal of worn United States paper currency from circulation.

Various laboratory methods of wearing the paper have been tried, such as the conventional folding and bending tests, the rotating-drum tumbling apparatus, and several specially devised methods of twisting, rubbing, and bending the paper. Of the various types of treatment used, crumpling the paper seems best to simulate the type of wear which the notes undergo in circulation. It also wears the test specimen fairly uniformly over its entire surface, and has in this respect a distinct advantage over the other wear tests that were studied. The creasing pattern and general appearance of worn-out paper currency are fairly well simulated by the random creasing which occurs in the crumpling operation.

The paper which has been used in this work is a special issue of nondistinctive, currency-type paper, similar to the regular issue, except that the distinctive, colored fibers have been left out. The paper was printed in the usual manner with a specially engraved plate.

II. CRUMPLING CYCLE

A definite procedure, involving mechanical aids, seems necessary in order to make the crumpling treatment reproducible. Considerable

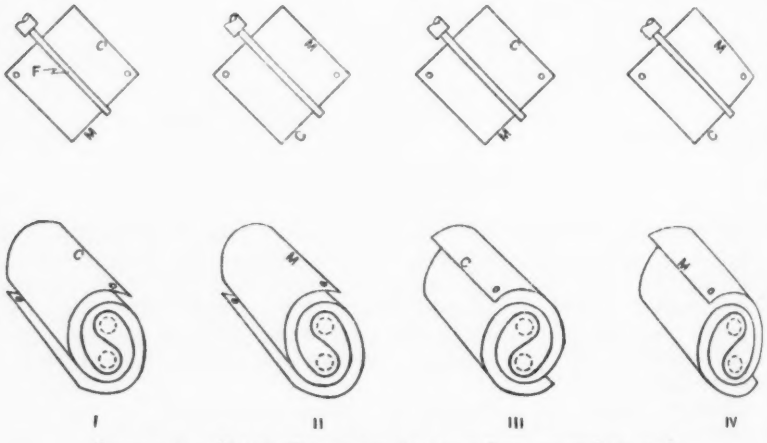

FIGURE 1.—*Sketch illustrating the four-phase crumpling cycle.*

C and *M* designate two edges parallel respectively to the cross direction and the machine direction of the paper. I and III are crushed in the cross direction; II and IV in the machine direction. III and IV are rolled (by the fork, *F*) in the opposite direction from I and II. The lower sketches are much enlarged over the upper ones.

experimenting with various crumpling procedures and mechanical models resulted in the choice of a procedure and crumpling cycle wherein a square of paper is rolled up, slipped into a hollow cylinder,

and crushed endwise of the roll to a predetermined volume by means of a piston. This crumpling procedure is repeated, with variations in a definite order, as many times as may be required. The crumpling cycle, involving four combinations of the directions of rolling and crumpling, is illustrated by figure 1.

The specimen 2⅝ inches on a side (the largest square obtainable from the present paper currency), is rolled, S-shaped, from the center by a two-tined fork, *F*, placed astride the specimen parallel with one or the other (alternately) of the two principal directions of the paper. As a result the paper roll is crushed by the piston, one time in the cross direction and the next time in the machine direction. Furthermore, in the first two phases of the cycle the fork is rotated in one direction and in the third and fourth phases it is rotated in the opposite direction. Bending the paper thus in opposite directions helps to break up preceding patterns of wrinkles and promotes a more even distribution of the creases.

Tests were made also with the simpler two-phase cycle (I and II only of figure 1), in which the specimen is crushed alternately in the machine direction and the cross direction, but is always rolled up in the same direction. It was somewhat surprising to find that the effect produced in this way by a given number of crumplings was only about half as great as that resulting from the four-phase cycle. The latter appears to promote a more general distribution of the creases, and, although somewhat complicated, produced such good results in the early experiments that the further development of this form of test seemed amply justified.

III. CRUMPLING APPARATUS

The crumpling cycle shown in figure 1 is accomplished by an automatic, motor-driven crumpling apparatus, illustrated by figures 2, 3, 4, and 5. A simpler, manually operated crumpling device was used in the earlier work, but the difficulty of preserving the necessary sequence in the various manipulations in the cycle led to the development of the automatic apparatus.

In the crumpling apparatus the specimen is secured by means of cords passed through eyelets placed in two opposite corners of the specimen, as shown in figure 2. The square of paper is rolled up by the fork, *F*, after which it is drawn into the crumpling cylinder, *C*, and crumpled to a small wad between the gate, *G*, and the piston, *P*. In subsequent operations the wad is expelled and opened out by the tension lever, *T*, and the smoothing arms, *A1* and *A2*, again rolled up and crumpled in the opposite direction, and so on according to the cycle illustrated in figure 1. A more detailed description of the operation and function of the various mechanisms will make the process clearer.

Figure 2 shows schematically the most important features of the apparatus. All the mechanisms that perform the various manipulations incident to the rolling, crumpling, and straightening of the specimen require intermittent motions. The mechanisms are, therefore, driven and timed by suitably shaped cams that operate on appropriate levers and linkages. The cams are mounted on a common shaft, *S1*, which is driven at about 7 revolutions per minute by

a motor and reducing gear (see fig. 3). The specimen is crumpled once each revolution of the camshaft.

At the beginning the fork, *F*, is in the broken-line position astride the tension cord, *H*, and out of contact with the specimen, *W*. The specimen, freely suspended under slight tension, tends to stand in a vertical plane. It is so constrained by the cord that joins the specimen to the piston—a horizontal, V-shaped loop, *V*, with its ends attached at the two ends of a diameter of the piston and its

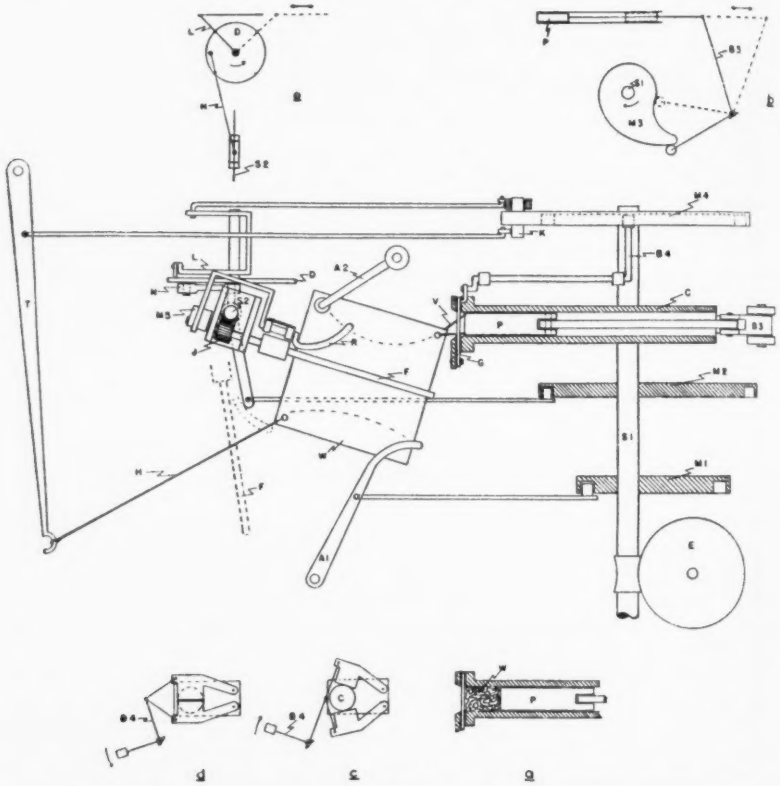

FIGURE 2.—*Schematic drawing of the automatic crumpling apparatus.*

apex in the eyelet. As the fork, *F*, swings about the vertical shaft, *S2*, as a pivot, approaching the corner of the specimen from its broken-line position, a curved finger, *R* (see also fig. 4), moving above the cord, *H*, carries the upper half of the specimen backward, forcing it toward the horizontal position. The fork then follows across the corner, astride the specimen to the middle, as shown by the full-line position in figure 2. In this position the fork stops its swing momentarily and begins to rotate. As the specimen is rolled up, the tension is relaxed, and the fork swings the roll into line with the crumpling cylinder. Friction plates, *Z* (figs. 4 and 5), flanking the fork above and below, aid in holding the specimen tightly rolled. The swing of the fork during this time is governed by a cam, *M2*, acting through appropriate linkage, while its rotation is produced by

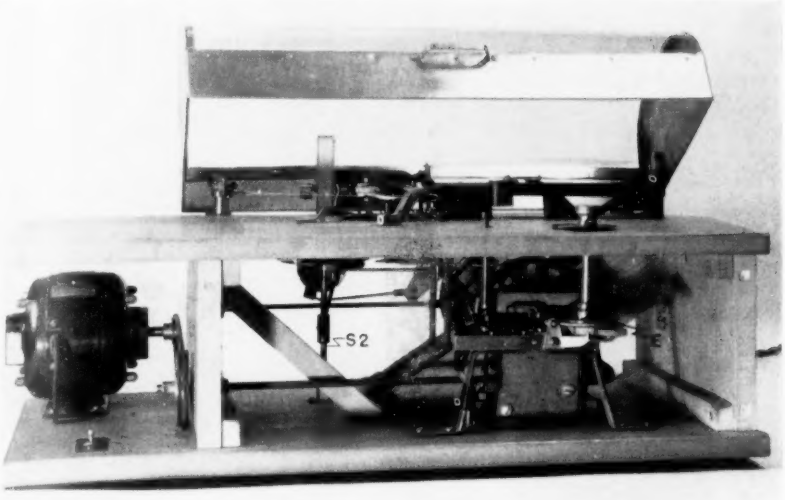

FIGURE 3.—*Automatic crumpling apparatus, showing the driving mechanism.*

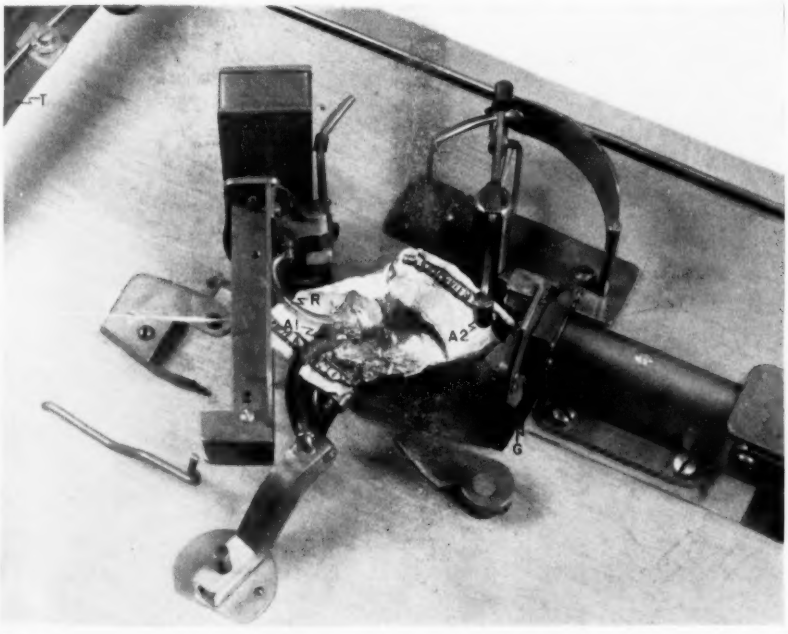

FIGURE 4.—*Detail of crumpling apparatus, showing specimen being prepared for the next crumpling.*

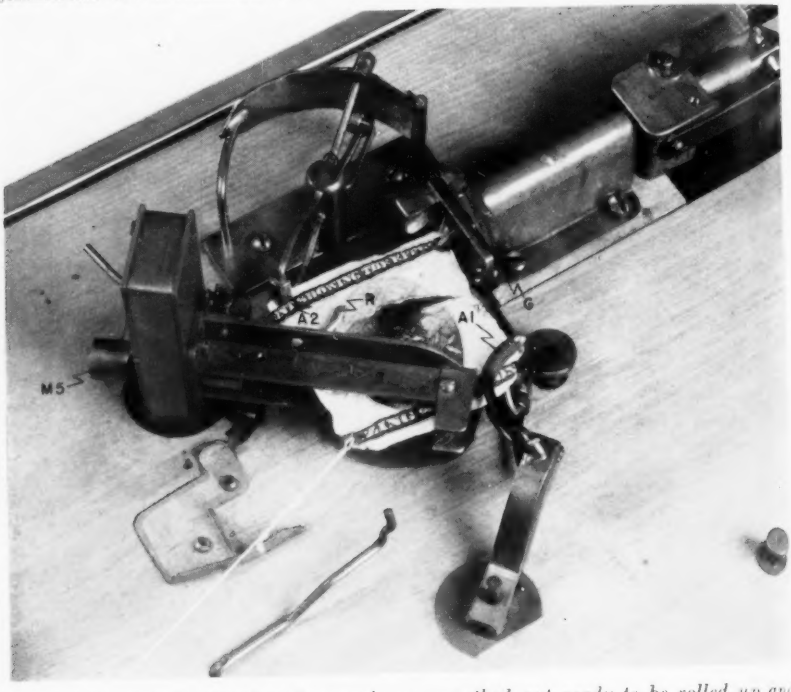

FIGURE 5.—*Detail showing the specimen smoothed out ready to be rolled up and crumpled again.*

a vertically moving rack (integral with *S2*) which turns a pinion, *J*, on the fork shaft.

At this point the piston is retracted, pulling the rolled specimen off the fork and into the crumpling cylinder through the funnel-shaped mouth. A scissorslike gate, *G*, closes behind the roll. On the forward stroke of the piston the specimen is slowly crumpled to a small wad, as indicated in *a* of figure 2. In the meantime the fork has swung back to its initial broken-line position. The movement of the piston is governed by a cam, *M3*, acting on a bell-crank lever, *B3*, as shown in *b* (reduced scale) of figure 2, and a quick-acting return mechanism, not shown. The opening and closing of the gate, *G*, are governed by a cam, *M4*, which acts through the offset bell-crank lever, *B4*, and a toggle. The gate is shown open and closed in *c* and *d* of figure 2.

After the specimen has been thus crumpled, the gate opens and the crumpled wad of paper is expelled as the piston stroke is completed. The tension lever, *T*, actuated by the crank-pin, *K*, on the cam, *M4*, exerts tension and stretches the crumpled paper out along the eyeleted diagonal. As the fork swings forward the second time, the reversing finger, *R*, comes underneath the cord and therefore turns the specimen about the eyeleted diagonal in the opposite direction to that of the first time. It is obvious from figure 1 that this will reverse the relative positions of machine direction and cross direction. Whereas in the first phase of the cycle the cross direction was the axis of the rolled specimen, now the machine direction is the axis and becomes the direction of crumpling in the second phase. In this manner the apparatus alternates the direction of crumpling in successive phases of the cycle. Cam *M5* on the fork shaft causes the reversing finger, *R*, to be one time above the cord and the next time below it, inasmuch as the fork makes 1½ revolutions each time the specimen is rolled up.

Following immediately behind the reversing finger, *R*, when it turns the specimen, as smoothing arm, *A1*, composed of two opposed jaws slightly ajar, moves over the eyeleted corner and along an arc to the adjacent uneyeleted corner, opening out the crumpled paper as it goes. Simultaneously a somewhat similar smoothing arm, *A2*, moves from the other eyelet on an arc to straighten out the opposite edge. As the smoothing clamps approach the uneyeleted corners, they begin to close by wedge action, until finally they clamp slightly and stretch the specimen out along the uneyeleted diagonal while tension is still on the other diagonal (fig. 5). Thus the crumpled paper is flattened out and held, allowing the fork to move freely into position to roll it up again. The smoothing arm, *A1*, is actuated by a cam, *M1*. The two smoothing arms are connected by a cross link (not shown), so that *A2* is driven by *A1*. The design of successful smoothing arms proved to be the most obdurate problem in developing the crumpling apparatus. At some stage in the crumpling cycle a persistent fold would usually appear that the mechanism was incapable of smoothing out sufficiently to allow the fork to function normally in the next phase. Many forms of smoothing devices were tried before a successful combination was found. The smoothing arms *A1* and *A2* differ somewhat in form and operation. Figures 4 and 5 show them in different positions.

The third and fourth phases in the cycle are like the first and second, respectively (see fig. 1), except that the fork turns in the opposite direction. This reversal in direction of rotation of the fork every second phase in the cycle is accomplished by reversing the direction

of travel of the rack and shaft, *S2*. This rack-and-shaft combination is moved up or down by a connecting rod, *N*, and a crank-pin attached to a disk, *D* (see *e* of fig. 2, and fig. 3), that makes a quarter turn for each revolution of the cam shaft, *S1*. Thus the rack is pushed upward during two successive phases in the cycle and downward during the next two. A ratchet device, *L*, actuated by the crank-pin, *K*, on the cam, *M4*, moves the disk a quarter turn for each revolution of the cam shaft, *S1*.

A disk counter and automatic stopping device, *E*, is geared to the cam shaft, *S1* (see also fig. 3). It can be set so that it will stop the motor after any predetermined number of crumplings in multiples of 4, from 4 to 100, by automatically throwing a toggle switch.

Although the apparatus is by no means infallible, it performs satisfactorily, and has been used in determining the probable relative wearing quality of many samples of currency paper.

IV. MEASURING THE EFFECT OF CRUMPLING

1. STRENGTH

Reproducible crumpling of the paper having been achieved, there follows the necessity of measuring the effect produced, and of measuring it in such a way as to be indicative of the probable behavior of the currency during its serviceable life. Several measurements suggest themselves as important criteria of change in significant properties as a result of the artificial wear treatment.

The change in strength of the paper is significant, although not of primary importance in the currency paper used today, inasmuch as improvements in making the paper, worked out several years ago by the National Bureau of Standards with the financial support and cooperation of the Bureau of Engraving and Printing, have resulted in a paper of such strength and durability that rupture of the paper is now not often the cause of retiring paper currency from circulation.

The easiest test of strength to make is, of course, the bursting-strength test. Unfortunately, it has not proved to be very useful, because the decrease in strength with repeated crumpling is accompanied by an increase in stretch. In the bursting-strength test these two trends offset each other, so that the bursting pressure does not change very much with the extent of the crumpling treatment.

The tensile strength does decrease considerably, and in a characteristic manner. Although it is a destructive test and cannot be used to follow the behavior of a given specimen through successive crumplings, it has been used to a considerable extent as a corroborative test of the end result of a series of crumplings. The square specimen is cut into four strips running in the crosswise direction, which are tested on a conventional paper tensile tester. The sum of the breaking loads for these four strips is taken to represent the strength of the worn specimen, and when divided by the width of the specimen represents the strength per unit width. With such a small square of paper it is not practicable to determine the tensile strength in more than one direction of the paper. The cross direction of the paper has been tested throughout the experimental work, since this direction runs lengthwise of the paper currency. Table 1, in which the tensile strength is expressed in kilograms per centimeter width, shows the manner in which tensile strength decreases with crumpling.

TABLE 1.—*Effect of crumpling on the tensile strength of currency paper*

Number of times crumpled	Tensile strength
	kg/cm
0	5.2
8	3.9
16	3.5
24	3.3
32	3.1
40	2.9

2. STIFFNESS

Another property which is altered significantly in worn paper currency is stiffness. In fact, the crispness of a new note, in contrast with the limpness of a much worn one, is one of the characteristics uppermost in the mind of anyone handling paper currency. A survey made several years ago of worn paper currency in several localities indicated that the limpness, measured as the amount of bending of the paper, supported as a cantilever beam bending under its own weight, correlated fairly well with the extent of unserviceability through wear in circulation as judged by United States Treasury experts. An obvious advantage of a stiffness test is that it can be made without destroying or injuring the specimen.

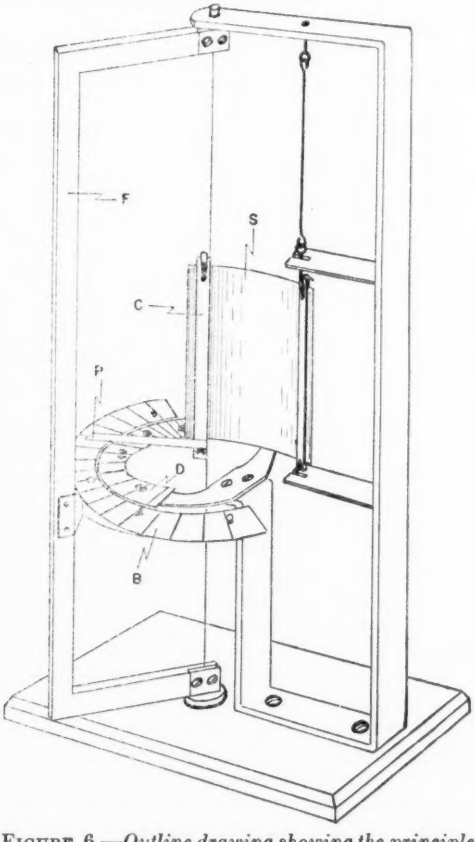

FIGURE 6.—*Outline drawing showing the principle used in measuring the stiffness of crumpled paper.*

Because of the shape and size of the specimen that must be tested, the conventional forms of stiffness testers are not very well suited to the purpose. A more appropriate form of apparatus was designed, and a homespun model was made with which some experimental tests could be performed. Figure 6 illustrates the principle used in the apparatus. A clamp, *C*, is suspended between two pieces of fine piano wire held by a pivoted frame, *F*. A similar clamp

is suspended from the fixed frame so that it can rotate freely through a small angle, or move in or out in the guides, to allow the specimen, S, to bend freely and naturally when clamp C is rotated. Swinging the frame, F, to right or left about the piano wire as an axis tends to rotate the clamp, C, and hence to bend the specimen. A pointer, P, on the clamp, C, shows on the fixed scale, D, the angular deflection of the specimen. The bending moment is measured by the torsion in the piano wire, and is indicated by the position of the pointer above the scale, B, attached to the frame, F.

Tests were made at various crumpling intervals to determine the amount the paper would bend under the influence of a constant bending moment. Thus, increasing values with successive crumplings would indicate the rate of increase in limpness with repeated crumpling. Some results are shown in table 2 for a given bending moment acting so as to bend the paper alternately to right and left of the zero position.

TABLE 2.—*Increase of limpness with crumpling*

[Angle through which paper is bent by a force of 0.5 g acting on a lever arm of 4 cm (distance between clamps)]

Number of times crumpled	Relative limpness	
	Right	Left
	Degrees	*Degrees*
0	3	3
1	2	2
2	4	5
3	3	3
4	7	3
8	9	6
12	14	8
16	12	9
20	19	15
24	23	12
28	35	14
32	40	23
36	48	23
40	27	24

Although the apparatus was amply sensitive for the requirements, the indicated decrease in stiffness is not very uniform. There were increases in stiffness during the first few crumplings, undoubtedly reflecting the structural stiffening lent by the crimping before the piece as a whole had become much weakened. Not until after the paper has been crumpled several times, therefore, will stiffness measurements indicate any wear at all. Table 2 shows also several instances farther along in the crumpling treatment when the stiffness appeared to increase temporarily. Another disturbing characteristic of this type of test is shown in the observation that, in reading the angle through which the paper is bent to right and left of the neutral position, the first determination made is usually the greater angle. This presumably means that the first reading is the better indication of stiffness (or limpness), and that when the paper is bent the pattern of crumples assumes a set such as to resist bending in the opposite direction. The crumpled paper seems to behave somewhat like a piece of distorted sheet metal, resisting bending up to a certain point and then suddenly snapping over into a new position. This sudden bending was frequently observed when the bending force was increased sufficiently.

The results of the stiffness tests indicate that, although an apparatus of this type might be developed into a very sensitive and significant measure of the stiffness of plane sheets, the measurement in this manner of the stiffness of crumpled paper is not very reliable. Hence the apparatus has not been further developed.

Another way of getting at the stiffness was also tried. The force required to open up the crumpled wad of paper appeared to be a possible means of evaluating the relative stiffness at various stages in the crumpling process. An attempt was made to make such a measurement in place on the crumpling apparatus by attaching a small spring balance to the cord that applies tension to the crumpled specimen. It was possible to make rough measurements, which were good enough to show significant changes. Some illustrative data are shown in table 3. This test has some promise, and may yet prove to be useful, but would require considerable refinement in order to be capable of accurate and dependable measurements.

TABLE 3.—*"Uncrumpling" force at various stages in the crumpling process*

Number of times crumpled	Uncrumpling force
	kg
2	4.3
6	3.4
10	3.2
20	2.2
40	1.3

3. AIR PERMEABILITY

(a) VALUE OF AIR-PERMEABILITY MEASUREMENTS

More sensitive than either the strength measurements or the stiffness tests, the increase in air permeability with crumpling has proved to be the most useful measure thus far found of the change resulting from the crumpling treatment. Although its relation to significant properties of the paper is somewhat indirect, the increase in air permeability appears to reflect to a very satisfactory degree the general deterioration resulting from wear. When paper is creased, the interlaced fibers are disturbed, and there is a partial breaking of the bonds which were formed on the paper machine and in subsequent processes in the manufacture of the paper. The hundreds of small creases that result from the crumpling of paper leave the specimen more open and more susceptible to the passage of air through the structure. Indirectly, this condition becomes a measure of the change in important characteristics of the paper. Loss in strength, increasing limpness, ability to absorb oil and grease, fuzziness of surface, susceptibility to catching dirt, and loss in the clarity of images printed on the paper, are all closely related to the loosening of the structure that is reflected in the increasing air permeability. An important advantage of this test is that it is nondestructive. Little or no change in the structure results from making the test. It is possible, therefore, for one to make repeated tests on the same specimen and to follow its behavior through a series of crumplings, noting the changes at all stages from new to completely unserviceable paper. The test is also very sensitive to small changes in structure.

Some typical graphs, illustrating the consistent and regular manner in which the air permeability increases as the crumpling process goes on, are shown in figure 7. The paper treated in this instance increased in air permeability considerably more than a hundredfold as a result of being crumpled 40 times, and the rate of increase is nearly linear. The data in figure 7 indicate that this kind of wear test is particularly suitable for appraising surface treatments and processing of currency paper. Curve *A* represents the rate of wear of a sample of the experi-

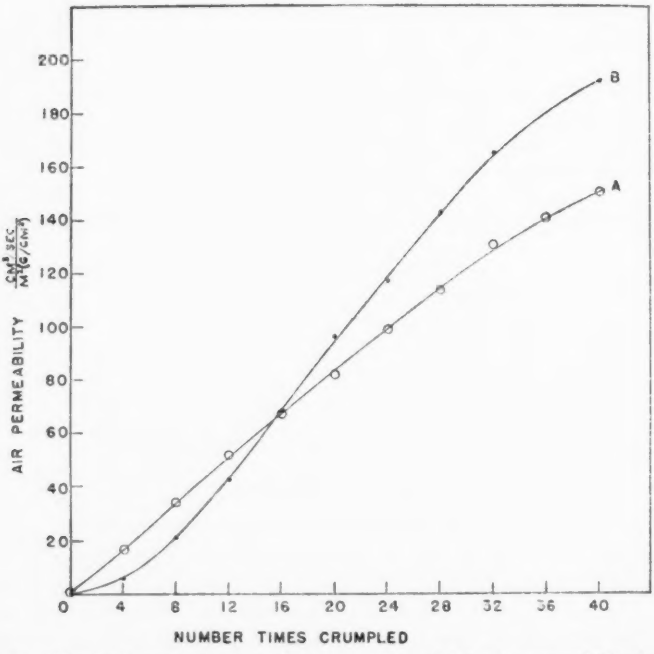

FIGURE 7.—*Typical curves showing the manner in which air permeability increases with repeated crumpling of paper.*

Air permeability is expressed as the number of cubic centimeters of air that pass per second through a square meter of the paper tested when impelled by a pressure difference of 1 gram per square centimeter (hereafter abbreviated to csm units).

mental, printed currency-type paper, while curve *B* represents the rate of wear of the same kind of paper after it has been coated with an experimental surface sizing material intended to increase its resistance to wear. During the early stages of the crumpling treatment the performance does appear to be improved by the surface sizing, but after a short time the treated paper begins to open up more rapidly, and during the remainder of the crumpling procedure it seems to wear more rapidly than the untreated paper.

In order that figure 7 may be more intelligible, it may be noted that the condition of currency paper after 40 crumplings represents an advanced stage of wear, although probably not in the neighborhood of complete unserviceability. Air-permeability tests have been made of a few silver certificates, which the Treasury Department had withdrawn from circulation, after periods of service ranging from 4 to 17

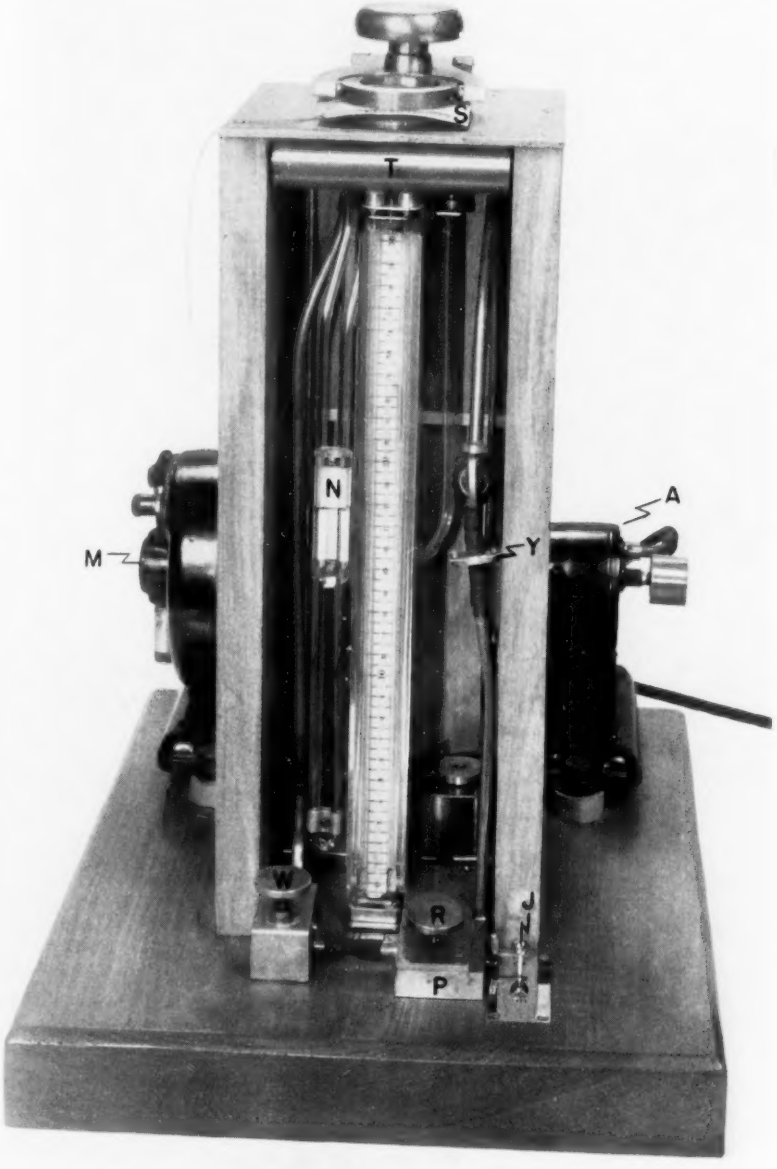

FIGURE 8.—*Air permeameter used as a means of measuring the break-down of the structure of paper resulting from the crumpling treatment.*

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months, because they were judged to be unserviceable. The air permeability of these silver certificates ranges from 78 to 787, with an average of about 350 csm [1] units.

(b) DESCRIPTION OF THE AIR-PERMEABILITY INSTRUMENT

An instrument was developed some time ago at the National Bureau of Standards, with which accurate measurements of the air permeability of paper can be made.[2] It will not, however, accommodate a specimen as small as that operated on in the crumpling apparatus. Preliminary tests were made with a small, improvised cell attached

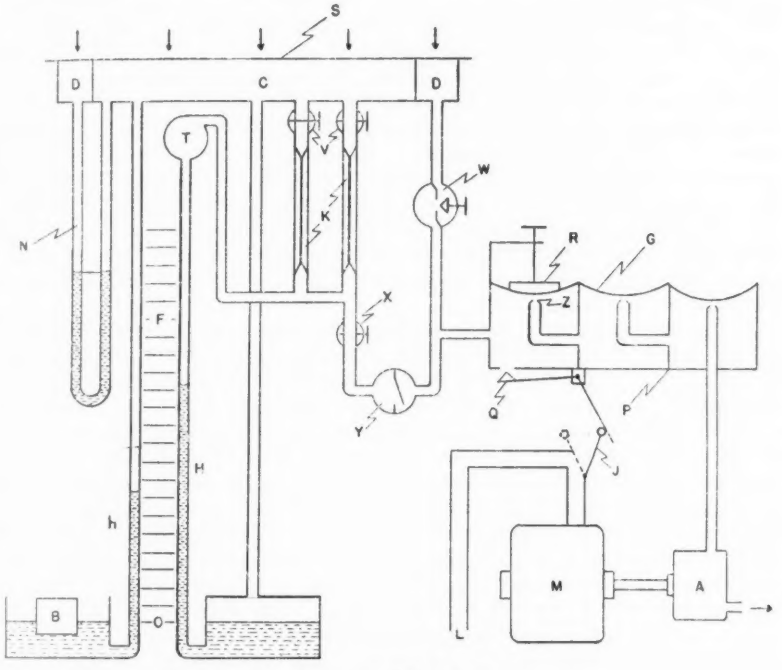

FIGURE 9.—*Diagram of the air permeameter.*

to this instrument. A new instrument, better suited to the requirements of the study of currency paper, has since been made. It is similar in general design to that described in RP681, but, since it differs from the older instrument in some respects, it will be described briefly. Figure 8 shows the instrument; figure 9 is a schematic diagram of it. The cell, much smaller than that in the older instrument, tests a 10-cm^2 area of the paper.

The specimen, *S*, is clamped over the permeability cell by means of a clamping ring (see fig. 8), the clamping pressure required being only enough to insure good contact of the specimen with the cell. Air is drawn by means of an air pump, *A*, through the specimen into the test cell, *C* (fig. 9), and simultaneously into an annular guard cell, *D*.

[1] A csm unit represents the flow of 1 cubic centimeter of air per second through 1 square meter of the material when the pressure difference across the sheet is 1 g/cm^2.

[2] F. T. Carson, *A sensitive instrument for measuring the air permeability of paper and other sheet materials*, BS J. Research **12**, 567 (1934) RP681.

The function of the latter is to prevent edge leakage into the test cell. When the air flow has been so adjusted by means of the valve, W, that the lateral pressure betweeen the two cells (shown by the manometer, N) remains zero, no edge leakage can occur. That part of the air that flows into the test cell through the specimen passes through one of a set of capillaries, K, which serves as the known resistance in a capillary flowmeter. From a previous calibration the rate of flow is known for any head, H, indicated on the flowmeter manometer, this rate of flow being the same as that through the specimen (with pressure head h).

The manometers, except N, are the single-reading type, composed of glass tubes attached to reservoirs at the base of the instrument. The reservoirs were made from large brass tubing. The glass-to-metal joints were made in the manner described in RP681, Thiokol gaskets being used. The manometer liquid is a light mineral oil, the specific gravity of which is accurately known. Before a test is made, while there is no pressure difference on the instrument, the zero of the scale, F, must be accurately set. The scale, common to the two manometers, can be moved up or down a small distance until the zero line is level with the bottom of the meniscus in the flowmeter manometer (when $H=0$). The meniscus in the other manometer is brought to the same level by raising or lowering a block of metal, B, partially submerged in the liquid in the communicating reservoir, which is open to atmospheric pressure.

A reading made on a manometer of this type is slightly less than the actual head, because the level in the reservoir sinks a little as the liquid rises in the tube. The resulting error in either reading is about one-half of 1 percent, since the inside diameter of each reservoir is about 14 times that of the glass tube connected to it. The accuracy of the calculated result does not suffer from this error, however, because small errors in these heads produce only second-order effects in the result, provided the ratio of the two heads is accurately known. This ratio is given by the ratio of the two readings H/h (inasmuch as each of these two readings involves the same percentage error). In calibrating the flowmeter, the actual heads were, of course, used.

The capillary tubes, K, communicate with the cell through petcocks, V, which are used to close off the capillaries not in use. These petcocks are more convenient than the tab valves formerly used, and have given no trouble from leakage. The capillaries are of glass, about 15 inches long, bent in a U-shape. As a means of measuring very small rates of flow, an extremely fine capillary, made of thermometer tubing, was added to the capillary flowmeter. Its use has not proved very satisfactory, however, because of the long time required for the pressure difference across it to settle down to a steady value. There has always been considerable uncertainty in its use.

A check valve, Y, is placed in the line to prevent a sudden backflow of air when the motor is cut off. Without such a valve a sudden reversal of flow sometimes forces all the liquid out of the flowmeter manometer into the connecting reservoir, together with some air. On its return the liquid traps air bubbles in the manometer tube, and these are sometimes troublesome to dislodge. The check valve is simply a perforated rubber disk in contact with a perforated metal disk, the two perforations being offset. This allows free flow of air in one direction; but when the pressure difference is reversed, so as to

press the rubber disk against the metal disk, the air leaks back slowly into the instrument.

A bypass valve, *Q*, is placed between the air pump and the flowmeter to lessen the chance of accidentally overflowing the manometer tubes or draining the manometers by suddenly throwing a large pressure difference on the instrument. When the current to the motor, *M* (line wires indicated by *L*), is cut off by throwing the switch, *J*, the bypass valve is kicked open. When the switch is again closed, the valve, *Q*, remains open until it is closed by hand. While it is open, air is drawn directly from the atmosphere instead of through the instrument. As a further precaution against contaminating the capillaries with manometer liquid, an overflow reservoir, or trap, *T*, is placed between the flowmeter manometer and the capillaries.

The pulsating and somewhat irregular pressure difference produced by the air pump is made steady across the instrument by interposing a pressure regulator, *P*, a different form of which was described in RP681. The use of fixed nozzles has somewhat simplified the new regulator, which is, however, in three stages instead of two. Three wells in a block of metal contain the nozzles. A sheet of thin rubber, *G*, held by a cover plate (not shown), serves both as a gasket and as the regulating diaphragms for the three stages of the regulator. The pressure difference between the atmosphere and each of the three wells decreases progressively toward the instrument. The first two stages, next to the air pump, have permanent adjustments. In the lowest-pressure stage, next to the measuring instrument, however, the center portion of the diaphragm is moved toward or away from the nozzle, *Z*, by means of a screw-driven ring, *R*, in order to change the pressure difference across the instrument. This single adjustment has been found more convenient than the double adjustment in the older apparatus.

This small air-permeability instrument has been used to advantage not only in helping to evaluate the wear of currency paper, but has frequently made it possible to test small pieces of various other materials which could not be accommodated in the older instrument.

V. CONCLUSION

The instruments which have been described have proved to be very useful in evaluating the effects of various treatments of currency paper intended to make it more serviceable. Beyond this application (illustrated by fig. 7) the value of the wear test offers a fertile field for future investigation. It is felt that the crumpling treatment described is a very effective means of simulating the type of wear to which currency paper is subjected, and perhaps also of artificially wearing various papers that are subjected to creasing and much handling. However, the problem of appraising the effect of crumpling (as of wear in actual service), and assigning numerical values that represent the degree of wear, is somewhat formidable when papers are involved which differ materially in type, composition, and structure. It has already been pointed out that the interpretation of air-permeability data in terms of wear is highly inferential. Although the test has worked out well in the application which has been made, it does not follow that the wear test can be extended unmodified to all kinds of

paper. When there are large differences in the initial air-permeability values of the papers to be compared, the significance of air permeability becomes somewhat entangled in the conflicting inferences that are possible. The development of additional criteria for the effect of the crumpling treatment seems, therefore, a likely corollary of the effort to extend the wear test to paper in general, and possibly even to the application of the test to currency-type papers that differ substantially in fiber composition or structure.

A more immediate problem is to determine the effect of common variable factors in the crumpling treatment so that the procedure may be standardized more effectively. The effects of relative humidity, rate of testing, and intensity of crumpling are outstanding examples of numerous influences about which more knowledge is required.

Work is continuing on various aspects of the standardization and the usefulness of the wear test.

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RESEARCH PAPER RP1391

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ANALYSIS OF DENTAL AMALGAMS CONTAINING MERCURY, SILVER, GOLD, TIN, COPPER, AND ZINC

By Harold J. Caul [1] and Irl C. Schoonover

ABSTRACT

The procedure provides for the separation and determination of gold, silver, mercury, tin, copper, and zinc in dental amalgams. The chief feature of the procedure is the simultaneous titration of silver and mercury with thiocyanate. It is this feature which makes the method particularly applicable for the analysis of smaller samples, for example, sections of restorations removed from teeth.

Briefly the method is as follows: The alloy is decomposed with nitric acid and tin is removed from this solution as metastannic acid. If gold is present, it will accompany the tin precipitate and is separated by converting the tin to soluble stannic sulfate. Silver and mercury are collectively titrated with thiocyanate, after which the thiocyanate precipitates are destroyed with nitric and sulfuric acids. The silver is precipitated as the chloride from this solution. The mercury is determined from the thiocyanate titration and the silver determination. Copper and snbsequently zinc are precipitated as sulfides at the proper acidities.

Simplifications of the procedure are presented for use when the composition of the silver alloy is known or when a partial analysis for silver and mercury alone is desired, as is often the case in control work.

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I. INTRODUCTION

The physical properties of dental amalgams depend to a large degree upon the amount of mercury in the hardened alloy. In dental practice, the methods employed for the preparation and insertion of

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amalgam fillings are so variable that it is doubtful whether any two fillings have precisely the same chemical composition, particularly with respect to mercury. Furthermore, some techniques are such that the composition of the amalgam may vary in different sections of the restoration. Such variations may well be responsible for some of the failures encountered in the use of amalgam.

Many techniques have been described in the dental literature for standardizing both amalgamation and methods of packing. Because there has been no convenient chemical method for determining the composition of an amalgam restoration, it has been difficult to study the effect of composition upon its physical properties and the effect of amalgamation and packing techniques upon the composition of the amalgam. Methods in which the composition is determined by weighing the mercury and alloy taken and the mercury removed during packing are rough approximations at best. Certainly no information can be obtained concerning the variations in the distribution of the mercury throughout the alloy by such methods.

It is the purpose of this paper to describe a rapid and convenient procedure for determining the mercury, silver, tin, copper, zinc, and gold in dental amalgams. The chief feature of the method is the simultaneous titration of silver and mercury with thiocyanate after the removal of tin. It is this feature which makes the method particularly applicable for use in the analysis of smaller samples, for example, sections of restorations removed from extracted teeth where nonuniformity in chemical composition is suspected. Methods in which mercury is determined on a separate portion are not applicable for the small samples which are usually available from dental restorations, because of the necessity of crushing, grinding, and using all the available material for one determination.

The procedures described for the separation of tin and gold and the determination of copper are essentially those described by Gilchrist [1],[2] as is also the procedure for determining end points of indicators in colored solution.

II. RECOMMENDED PROCEDURE

1. SOLUTION OF SAMPLE

Place a 0.2- to 0.3-g sample in a 250-ml beaker, add 10 ml of nitric acid (sp gr 1.42), cover and set on the steambath. After the brown fumes disappear and disintegration of the alloy is complete, remove the cover glass and evaporate to incipient dryness. Add 5 ml of freshly boiled nitric acid. Digest 5 minutes on a steambath and dilute with water to 60 ml. Digest 1 hour on a steambath. All the constituents go into solution except tin and gold. Tin will be present as a white precipitate of metastannic acid. Gold, if present, imparts a red or purple color to the precipitate.

2. DETERMINATION OF TIN IN THE ABSENCE OF GOLD

If a precipitate of metastannic acid is obtained by the procedure above, catch it on a 9-cm filter paper of close texture, which contains some paper pulp. Wash the filter and precipitate thoroughly with hot water which is acidified with sulfuric acid between the limits of

[2] Figures in brackets indicate the literature references at the end of this paper.

pH 4 (end point of bromphenol blue) and pH 1.5 (red-yellow end point of thymol blue). Reserve the filtrate and washings for the determination of the remaining constituents. Ignite the precipitate of metastannic acid carefully in a porcelain crucible until carbonaceous matter is eliminated, and finally ignite the residue between 1,100° and 1,200° C, for one-half hour, taking care that the flame of the burner does not envelop the crucible. Weigh the residue, which should be white when cold, as stannic oxide, SnO_2. Calculate its tin content with the theoretical factor 0.7877.

3. DETERMINATION OF TIN AND OF GOLD

If gold is present, the procedure for the determination of tin must be modified as follows. Return the filter and precipitate of metastannic acid and gold (section II–2) to the beaker in which the tin was precipitated, add 5 ml of sulfuric acid (sp gr 1.84), and destroy organic matter by repeatedly adding nitric acid and subsequently heating to the fuming point of sulfuric acid. The tin precipitate goes into solution, leaving behind the gold, somewhat agglomerated. Cool, dilute the concentrated acid solution to 50 ml with distilled water, and, because of the instability of stannic sulfate, keep it cool and filter immediately through a thin 7-cm paper of close texture. Wash the filter paper and its contents thoroughly with cool diluted sulfuric acid (1+99). The recovered gold is ignited and weighed as metal. Dilute the solution of stannic sulfate to 200 ml and set on a steambath for 1 hour. Catch and wash the resulting precipitate of metastannic acid as described in section II–2. Discard the second filtrate and washings.

4. COMBINED TITRATION OF MERCURY AND SILVER WITH AMMONIUM THIOCYANATE

Transfer the reserved filtrate and washings (a volume of 200 ml or less) from the tin determination obtained in II–2 to a 600-ml beaker; add a 5-percent solution of potassium permanganate dropwise until the solution remains pink for 5 minutes or more. Add small crystals of ferrous sulfate to destroy the excess permanganate. Add 4 ml of a saturated solution of ferric ammonium sulfate which has been decolorized by the addition of nitric acid. Cool the solution to a temperature below 15° C and titrate with a standardized ammonium thiocyanate solution[3] (approximately 0.05 *N*) until a distinct and permanent pink color is obtained. The solution must be stirred vigorously near the end point. This titration represents the total mercury and silver and will be used as a basis for the determination of mercury (section II–6).

5. DETERMINATION OF SILVER

To the solution containing the precipitates of mercury and silver thiocyanates add 10 ml of sulfuric acid (sp gr 1.84) and evaporate to the fuming point of sulfuric acid. Cool, add 5 ml of nitric acid (sp gr 1.42), and again evaporate to the fuming point of sulfuric acid. Repeat this procedure at least two times in order to decompose the

[3] The ammonium thiocyanate solution may be standardized with pure mercury or silver. The mercury or silver should be dissolved as recommended in II–1, diluted to 200 ml, and then titrated as described in II–4.

thiocyanate. Dilute with distilled water to 300 ml and digest on a steambath until the salts are in solution. Filter to remove any silica and add to the filtrate 10 ml of diluted hydrochloric acid (1+9), digest on a steambath until the silver chloride has coagulated, cool to room temperature, and filter through a glass filtering crucible of fine porosity. Wash the beaker and precipitate with cool diluted nitric acid (1+300). Dry the precipitate in an oven at 120° to 130° C for 1 hour. Cool and weigh as silver chloride. Calculate the weight of silver as metal with the factor 0.7526.

6. DETERMINATION OF MERCURY

From the weight of silver determined calculate the milliliters of standard thiocyanate required to react with the silver to form silver thiocyanate (AgCNS). The difference between the total thiocyanate used (section II–4) and that required to precipitate the silver will represent the thiocyanate required to react with the mercury to form mercuric thiocyanate, $Hg(CNS)_2$.

7. DETERMINATION OF COPPER

Transfer the filtrate and washings from the precipitation of silver chloride (section II–5) to a 600-ml beaker and evaporate to the fuming point of sulfuric acid. Cool, wash the sides of the beaker, and again evaporate to the fuming point of sulfuric acid. Cool, dilute with distilled water to 400 ml, and digest on a steambath until the salts are in solution. Filter to remove silica. Heat the solution on a steambath to approximately 85° C, and precipitate the copper and mercury by passing in a stream of hydrogen sulfide for 30 minutes. Filter the solution immediately through an 11-cm paper of close texture and wash the filter and precipitate thoroughly with cool diluted sulfuric acid (1+300) which is saturated with hydrogen sulfide. Dry the filter and precipitate and ignite them carefully in a porcelain crucible in a hood (mercury is volatilized during ignition). Too rapid ignition causes the sulfide to melt, with danger of mechanical loss by spattering. Wipe down the walls of the crucible with a piece of moistened ashless filter paper and then ignite the residue in air and finally in hydrogen. Cool the reduced metal in hydrogen and weigh it as metallic copper.

8. DETERMINATION OF ZINC

The zinc is precipitated as the sulfide from a buffered solution, as described by H. A. Fales [2].

Evaporate the filtrate and washings from the precipitation of copper and mercury to 50 ml or less. Neutralize with diluted ammonium hydroxide (1+1) to the red-yellow end point of thymol blue [4] (about pH 1.5). Add 25 ml of a 20-percent solution of citric acid and neutralize to the yellow-blue end point of bromphenol blue (about pH 4). Add 25 ml of "formic mixture" (200 ml of formic acid, 90 percent; 30 ml of ammonium hydroxide, sp gr 0.90; and 200 g of ammonium sulfate diluted to 1 liter with distilled water) and 20 ml of formic acid

[4] Because the solutions are colored by iron, a procedure recommended by Gilchrist [1] was used for determining the indicator end points. A drop of the indicator (0.01 percent) is permitted to react with a drop of the solution on the end of a stirring rod.

(90 percent). Dilute to 200 ml. Precipitate the zinc by passing in a stream of hydrogen sulfide for 1 hour. Let the solution stand 2 hours and filter through a paper of close texture. Wash the filter and precipitate thoroughly with a diluted formic acid solution (1+250) which is saturated with hydrogen sulfide. Without removing the filter or precipitate from the funnel, dissolve the precipitate by successive washings with hot diluted hydrochloric acid (1+1). Evaporate to 5 ml and dilute to 50 ml. Adjust the acidity, reprecipitate, and wash the precipitate as before. Carefully ignite the precipitate and paper in a porcelain crucible with a final temperature between 950° and 1,000° C for one-half hour. Weigh as zinc oxide and calculate the weight of zinc as metal with the factor 0.8034. Blank runs must be carried through all the steps of this zinc procedure because of the large quantities of reagents used.

III. DISCUSSION OF THE METHOD

1. PREPARATION AND SOLUTION OF THE SAMPLE

If an amalgam restoration which has been in service is to be analyzed, it is essential that surface tarnish and coatings be removed. This can be done by using a fine file or dental burr operated in such a manner as to prevent local heating and loss of mercury.

No loss of mercury will occur through volatilization if the sample is dissolved in nitric acid as recommended. Weighed samples of pure mercury and mercury-silver mixtures were dissolved in nitric acid and evaporated to dryness on a steambath. When the samples were titrated with thiocyanate, the results were correct for both silver and mercury. See experiments 3, 4, 5, 6, and 7 in table 1.

2. INTERFERING ELEMENTS

Chlorides, bromides, or iodides interfere when the thiocyanate titration is made. These elements form precipitates with silver and complex salts with mercury which would give a low titer. Bromides and iodides would also interfere with the silver chloride determination.

Cuprous copper and mercurous mercury interfere with the thiocyanate titration because they form insoluble thiocyanates. They must be oxidized as indicated in the procedure.

Oxides of nitrogen interfere because they decompose the thiocyanate ion. The solution obtained by dissolving the sample in nitric acid is evaporated to dryness for this reason. Freshly boiled nitric acid should be used where indicated.

3. THIOCYANATE END POINT

The color change in the combined titration of silver and mercury with thiocyanate is sharp and can be readily obtained if the solution is maintained below 15° C and is vigorously stirred near the end point. Titration should be continued until a permanent and distinct rose-brown color is observed. A slight straw color is often observed before the end point; this should not be mistaken as the end point. The rose-brown color can best be observed by permitting the precipitate to settle and observing the color through the supernatant liquid.

4. SIMPLIFICATION OF PROCEDURE FOR CONTROL WORK

The foregoing procedure may be simplified and shortened when an approximate analysis is desired. For example, entire specimens or sections of specimens on which physical tests have been made can be weighed and dissolved as described in II–1. The mercury and silver are simultaneously titrated with thiocyanate without removing the metastannic acid precipitate. From this value and a knowledge of the silver content of the original alloy (determined by titrating a weighed sample with thiocyanate), the amount of mercury or silver in the amalgam may be calculated from the following equations.

Equation 4 is used to calculate the amount of silver. This value for silver is used in eq 3 to calculate the mercury.

In the following equations

a=percentage of silver in the silver alloy divided by 100.
b=weight (mg) of sample of amalgam.
Hg=weight (mg) of mercury in the amalgam.
Ag=weight (mg) of silver in the amalgam.
S=weight (mg) of silver alloy in the amalgam.
N=normality of the ammonium thiocyanate solution.
ml=the volume (ml) of thiocyanate used for the titration.

$$\frac{Hg}{100.3}+\frac{Ag}{107.88}=N\,ml \tag{1}$$

$$Hg+Ag+\left(\frac{1-a}{a}\right)Ag=b \tag{2}$$

$$Hg+Ag\left[1+\left(\frac{1-a}{a}\right)\right]=b$$

$$Hg+\frac{Ag}{a}=b$$

$$Hg=b-\frac{Ag}{a} \tag{3}$$

Substituting Hg in eq 1,

$$\frac{b}{100.3}-\frac{Ag}{100.3a}+\frac{Ag}{107.88}=N\,ml$$

$$\frac{Ag}{100.3a}-\frac{Ag}{107.88}=\frac{b}{100.3}-N\,ml$$

$$Ag=\frac{\frac{b}{100.3}-N\,ml}{\frac{1}{100.3a}-\frac{1}{107.88}}=\frac{0.009970\times b-N\,ml}{0.009970\times\frac{1}{a}-0.00927} \tag{4}$$

From eq 2

$$S=Ag+\left(\frac{1-a}{a}\right)Ag=Ag\left[1+\left(\frac{1-a}{a}\right)\right]$$

$$S=\frac{Ag}{a} \tag{5}$$

The weights of tin, copper, zinc, and gold can be calculated if the chemical composition of the silver alloy is known, from the weight of alloy used in the amalgam, as determined by eq 5.

The values from these calculations (eq 3, 4, and 5) will be subject to error caused by the small amount of the alloy removed with the excess mercury during packing. (See Souder and Sweeney [3].)

IV. EXPERIMENTAL RESULTS

The results of 19 experiments, performed in the development and verification of the recommended procedure, are compiled in table 1. Experiments 1 through 7 show the accuracy in titrating weighed portions of pure silver and mercury with ammonium thiocyanate. Experiments 8 through 17 illustrate the accuracy of separations involved in the analysis of dental amalgams. Experiments 18 and 19 demonstrate that mercury and silver may be titrated in the presence of metastannic acid with ammonium thiocyanate.

Table 2 illustrates the accuracy of the calculations used in the modified procedure. The data given for experiments 10 through 17 in table 1 were used for these calculations.

TABLE 1.—*Results illustrating the accuracy of the procedure*

Experiment	Mercury		Silver		Tin		Copper		Zinc	
	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered
	Grams	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*
1			0.1005	0.1004						
2			.1192	.1193						
3	0.0733	0.0733								
4	.2150	.2150								
5	.1143	.1140								
6	.1146	.1141	.1319							
7	.2275	.2272	.0666							
8	.0819	.0811	.1321	0.1321	0.0524	0.0524	0.0087	0.0089		
9	.0876	.0874	.1304	.1304	.0517	.0516	.0086	.0086		
10	.1824	.1822	.0535	.0534	.0208	.0209	.0035	.0035	0.0008	0.0009
11	.1170	.1170	.0348	.0345	.0135	.0138	.0023	.0024	.0005	.0002
12	.0826	.0827	.0567	.0562	.0221	.0224	.0038	.0039	.0008	.0008
13	.1070	.1070	.0727	.0726	.0284	.0283	.0048	.0048	.0011	.0012
14	.0663	.0665	.1073	.1072	.0418	.0412	.0071	.0075	.0016	.0019
15	.0565	.0566	.0900	.0897	.0351	.0348	.0059	.0060	.0013	.0015
16	.0115	.0119	.1495	.1492	.0583	.0587	.0099	.0100	.0022	.0020
17	.0172	.0176	.2215	.2212	.0863	.0866	.0147	.0147	.0032	.0031
18	.1596	.1596	.2211		.0876		.0145			
19	.1057	.1056	.2402		.0952		.0158			

TABLE 2.—*Calculations illustrating the accuracy of the modified procedure* [1]

[The composition of the silver alloy used in these experiments is: Tin, 26.5 percent; silver, 68.1 percent; copper, 4.5 percent; zinc, 1.0 percent]

Experiment	Sample of amalgam	Volume of ammonium thiocyanate [2] (NH_4CNS)	Silver		Mercury	
			Taken	Calculated	Taken	Calculated
	Milligrams	*Milliliters*	*Milligrams*	*Milligrams*	*Milligrams*	*Milligrams*
1	261.0	46.45	53.5	53.8	182.4	182.0
2	168.1	29.87	34.8	35.2	117.0	116.4
3	166.0	27.08	56.7	57.2	82.6	82.0
4	214.0	34.96	72.7	73.2	107.0	106.5
5	224.1	33.28	107.3	107.4	66.3	66.4
6	188.8	28.04	90.0	90.5	56.5	55.9
7	231.4	30.17	149.5	149.9	11.5	11.3
8	342.9	44.71	221.5	222.0	17.2	16.9

[1] These values were determined on experimental mixes of amalgam from which the excess mercury was not expressed and are, therefore, not subject to the error caused by the removal of small amounts of metal with the mercury normally expressed during packing.

[2] Ammonium thiocyanate (NH_4CNS)=0.0498 *N*.

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X-RAY STUDIES OF COMPOUNDS IN THE SYSTEMS PbO-B_2O_3 AND K_2O-PbO-SiO_2

By Howard F. McMurdie

ABSTRACT

X-ray diffraction data as determined from powder patterns of 10 compounds occurring in the systems PbO-B_2O_3 and K_2O-PbO-SiO_2 are published as a supplement to the phase equilibrium work previously reported on these systems. These data may be useful in related studies for identification of phases. The unit cell of $K_2O.2PbO.2SiO_2$ was determined and a possible atomic arrangement outlined.

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I. INTRODUCTION

Reports have been published on the systems PbO-SiO_2 [1],[1] K_2O-PbO-SiO_2 [2], PbO-B_2O_3 [3], and PbO–B_2O_3-SiO_2 [4] by the National Bureau of Standards. These phase equilibrium studies are of interest to investigators of lead glazes, enamels, and glasses. X-ray diffraction patterns have been reported for compounds in the system PbO-SiO_2 [5] and for the ternary compound, $5PbO.B_2O_3.SiO_2$ [4]. Since X-ray powder patterns of crystallnie phases aid in most investigations of these or related systems, it has been thought desirable to publish X-ray data for compounds in the systems PbO-B_2O_3 and K_2O-PbO-SiO_2. This present report completes the data pertaining to the patterns of all of the stable lead compounds so far mentioned in these four systems.

II. METHODS

The methods used in the preparation of the compounds and their identification by means of the polarizing microscope, together with the optical properties as measured by the microscope, have been given in the reports mentioned.

For the preparation of the powder patterns, the powdered samples were mounted on fine glass rods in the center of cylindrical cameras, having radii of about 5.7 cm, and were rotated during exposure. CuK_α radiation was used. The radii of the cameras were checked by

[1] Figures in brackets indicate the literature references at the end of this paper.

NaCl. The positions of the lines on the film were measured to 0.1 mm and the relative intensities were calculated.

III. RESULTS

In most cases the compounds are of such low symmetry that it is very difficult, if not impossible, to index the lines. However, one of the compounds ($K_2O.2PbO.2SiO_2$) is hexagonal and its unit cell has been measured.

Tables 1 to 6 give the interplanar spacings and estimated relative intensities for the following lead borates: $\alpha 4PbO.B_2O_3$, $\beta 4PbO.B_2O_3$, $\alpha 2PbO.B_2O_3$, $\beta 2PbO.B_2O_3$, $5PbO.4B_2O_3$, and $PbO.2B_2O_3$.

Tables 7 to 9 give similar data for three of the ternary compounds ($K_2O.4PbO.8SiO_2$, $K_2O.PbO.4SiO_2$, and $K_2O.2PbO.2SiO_2$) occurring in the system K_2O-PbO-SiO_2. Because of the instability of $2K_2O.PbO.3SiO_2$, an X-ray pattern was not made. The compound in table 10 designated as "unknown" is identical with that referred to in the original work on the system as a "fifth compound." Its composition has not been determined.

$K_2O.2PbO.2SiO_2$ crystallizes in hexagonal plates and is optically uniaxial. The pattern, represented by data given in table 9, was found to fit a hexagonal lattice with $a=5.62\pm0.02$ A and $c=7.57\pm0.02$ A. The spacings calculated for the various planes using these values are given in the last column. With one molecule to the unit cell, this size gives a calculated density of 5.25. The density determined by pycnometer was 5.15. Considering that the sample contained some glass, this is good agreement.

Study of the reflections present shows no regular halving; thus several space groups are possible. Intensity calculations on a few simple planes indicate that very probably the atoms are arranged as follows in C_{3i}^1:

2 K in 2 *d* (1/3 2/3 *z*) (2/3 1/3 $\bar{z}$) [6]	$z\approx0.5$
2 Pb in 2 *d* (1/3 2/3 *z*) (2/3 1/3 $\bar{z}$)	$z\approx0$
2 Si in 2 *c* (0 0 *z*) (0 0 $\bar{z}$)	$z\approx .28$
1 O in 1 *b* (0 0 1/2)	
6 O in 6 *g* (*x y z*) etc.	$z\approx .18$

Such an arrangement gives a structure consisting of two silica tetrahedrons with a single shared oxygen (at 0 0 1/2). The K and Pb atoms are each equidistant from six oxygen atoms. The x and y parameters for the oxygen atoms were not determined. If they have a simple ratio, it might result in the crystal having the symmetry of a higher space group, such as D_{3d}^1 or D_{3d}^3.

IV. SUMMARY

The X-ray diffraction patterns for 10 compounds occurring in the systems PbO-B_2O_3 and K_2O-PbO-SiO_2 have been determined. These can be used by workers in related studies for identification of crystalline phases. The unit cell of $K_2O.2PbO.2SiO_2$ was determined and a tentative structure outlined.

The author is grateful to E. N. Bunting for the preparation and identification of the specimens examined and for the determination of the density of $K_2O.2PbO.2SiO_2$.

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TABLE 1.—*Interplanar spacing of* α$PbO.B_2O_3$

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	d	Estimated intensity	d
	A		*A*
W	4.20	M	2.280
W	3.87	W	2.248
S	3.59	W	2.093
M	3.44	VW	2.070
M	3.34	VW	1.916
VS	3.12	VW	1.893
M	3.07	VW	1.854
M	3.00	S	1.799
W	2.94	M	1.769
S	2.86	VW	1.754
W	2.71	VW	1.735
VW	2.55	S	1.708
VW	2.435	M	1.659
W	2.379	S	1.646

TABLE 2.—*Interplanar spacing of* β4$PbO.B_2O_3$

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	d	Estimated intensity	d
	A		*A*
M	4.58	VW	2.075
W	3.92	M	1.955
W	3.79	M	1.890
VW	3.26	VW	1.868
VS	3.07	W	1.836
S	3.02	M	1.802
VW	2.94	VW	1.776
S	2.87	VW	1.750
M	2.75	VW	1.738
W	2.69	W	1.699
VW	2.63	VW	1.654
M	2.49	VW	1.632
VW	2.320	W	1.616
W	2.258	W	1.590
W	2.200	VW	1.558
VW	2.160	W	1.542

TABLE 3.—*Interplanar spacing of* $\alpha 2PbO.B_2O_3$

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	*d*	Estimated intensity	*d*
	A		*A*
VW	7.2	VW	2.56
M	5.81	S	2.40
VW	5.52	M	2.25
VW	3.90	W	2.09
VS	3.62	M	2.043
VS	3.39	M	1.984
M	3.26	S	1.951
VS	3.18	W	1.879
W	2.97	M	1.826
M	2.88	W	1.808
W	2.76	M	1.720
W	2.70	M	1.702
M	2.60	W	1.670

TABLE 4.—*Interplanar spacing of* $\beta 2PbO.B_2O_3$

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	*d*	Estimated intensity	*d*
	A		*A*
W	6.54	M	2.292
S	5.55	VW	2.242
VW	4.66	VW	2.200
M	3.67	W	2.155
M	3.52	S	2.034
S	3.42	VW	1.984
VS	3.05	M	1.943
S	3.00	VW	1.912
M	2.92	VW	1.894
M	2.82	W	1.868
M	2.78	W	1.826
M	2.74	W	1.805
W	2.56	W	1.760
W	2.53	W	1.741
W	2.49	W	1.714
VW	2.366	W	1.690

TABLE 5.—*Interplanar spacing of* $5PbO.4B_2O_3$

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	*d*	Estimated intensity	*d*
	A		*A*
VS	5.89	VW	1.905
M	4.86	VW	1.840
W	4.45	VW	1.809
S	3.70	VW	1.779
VS	3.39	M	1.738
VS	3.16	VW	1.696
VS	3.07	M	1.662
M	2.96	W	1.643
VW	2.83	M	1.591
W	2.71	W	1.549
W	2.60	W	1.519
VW	2.280	W	1.486
VS	2.185	M	1.451
S	2.070	VW	1.425
M	2.009	VW	1.395
S	1.936	W	1.371

TABLE 6.—*Interplanar spacing of* $PbO.2B_2O_3$

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	*d*	Estimated intensity	*d*
	A		*A*
S	5.46	S	1.890
S	4.12	W	1.854
S	3.96	M	1.805
S	3.07	M	1.729
M	2.96	M	1.690
S	2.80	W	1.667
S	2.75	VW	1.593
VS	2.68	S	1.556
W	2.314	W	1.535
W	2.231	W	1.521
VW	2.185	W	1.482
W	2.116	M	1.457
W	2.052	M	1.437
VS	2.026	W	1.406
M	1.975	W	1.393
S	1.939	W	1.375

TABLE 7.—*Interplanar spacing of* $K_2O.4PbO.8SiO_2$

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	*d*	Estimated intensity	*d*
	A		*A*
VS	8.32	W	2.079
M	6.59	W	2.061
M	5.89	W	2.009
VW	4.38	W	1.963
VW	4.20	VW	1.936
VW	3.96	W	1.795
W	3.73	M	1.760
VS	3.52	M	1.717
S	3.29	W	1.687
S	2.78	VW	1.670
S	2.71	W	1.614
VW	2.63	W	1.583
W	2.58	W	1.564
M	2.367	M	1.512
W	2.308	M	1.467
VW	2.263	M	1.439

TABLE 8.—*Interplanar spacing of* $K_2O.PbO.4SiO_2$

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	*d*	Estimated intensity	*d*
	A		*A*
S	6.22	VW	2.53
M	5.81	M	2.42
S	5.55	M	2.40
VW	5.20	VW	2.285
M	4.81	W	2.237
W	4.45	M	2.155
VS	3.70	VW	2.121
VW	3.50	VW	2.083
VW	3.33	VW	2.052
VS	3.22	W	2.021
VS	3.08	VW	1.959
S	2.99	VW	1.939
W	2.81	VW	1.912
W	2.76	VW	1.864
M	2.67	W	1.833
M	2.58		

TABLE 9.—*Interplanar spacing for* $K_2O.2PbO.2SiO_2$

[Based on $a=5.62$ A; $c=7.57$ A hexagonal lattice]

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	*d*	*hkl*	*d* (calculated)
	A		*A*
S	7.5	001	7.6
W	4.83	100	4.85
S	4.08	101	4.08
VS	2.98	102	2.98
S	2.80	110	2.80
M	2.62	111	2.63
VW	2.52	003	2.52
W	2.42	200	2.43
VW	2.314	201	2.32
M	2.237	103-112	2.242
S	2.043	202	2.040
M	1.893	004	1.893
VW	1.833	120	1.840
W	1.779	121	1.782
M	1.760	104	1.765
S	1.656	122	1.655
M	1.619	300	1.619
VW	1.578	301	1.582
W	1.568	114	1.568
VW	1.516	005	1.514

TABLE 10.—*Interplanar spacing of* K_2O-PbO-SiO_2 *compound of unknown composition* [a]

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	*d*	Estimated intensity	*d*
	A		*A*
S	8.32	VW	2.42
W	6.05	M	2.30
W	5.85	VW	2.23
VW	4.36	VW	2.165
VW	4.12	M	2.070
VS	3.51	W	1.996
W	3.18	M	1.939
W	2.95	W	1.833
M	2.84	M	1.729
M	2.74	S	1.703
M	2.65	W	1.618
W	2.51		

[a] This compound was reported as a primary phase in a small field adjacent to the silica field. It melts incongruently.

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SLOPES OF pv ISOTHERMS OF He, Ne, A, H_2, N_2, AND O_2 AT 0° C

By Carl S. Cragoe

ABSTRACT

The change of pv (pressure times volume of a constant mass of gas) with pressure or density at constant temperature and low pressures is treated as a characteristic physical quantity. Various methods of determining this quantity from available experimental data for several gases, including He, Ne, A, H_2, N_2, and O_2, are examined with special reference to the reliability of the values at 0° C.

Reliable values for these quantities are important for many purposes, such as correcting temperatures measured by means of gas thermometers to the thermodynamic scale and in the derivation of the absolute temperature of the ice point, T_0.

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I. INTRODUCTION

In many fields of science it is frequently possible to calculate a desired result in several different ways, sometimes employing the results of more than one set of measurements. In many cases it is found that such calculations lead to somewhat different results, depending upon the assumptions and auxiliary numerical values used to obtain a derived result. If great exactness is desired it is obvious that careful consideration should be given to the reliability of (1) each set of experimental data, (2) each result derived therefrom, (3) the various methods of calculation, and (4) the assumptions employed. This appears to be especially applicable to the derivation of some of the so-called fundamental or basic physical constants, which cannot

be obtained by direct measurement but must be obtained indirectly by calculation, using certain assumptions.

The numerical values of many basic physical constants which have been used for years are now in such an unsettled state that it is difficult for an unbiased person to decide which of the many published "recommended" or "accepted" values to use in his calculations. While this is particularly true in the case of the so-called atomic constants, it also appears to apply to what may be called thermodynamic constants, including the gas constant (R,k), the absolute temperature of certain "fixed points", such as the ice point, and the atomic or molecular weights of some of the simpler gases.

It is not the intention in this paper to derive additional "recommended" or "accepted" values for these constants but rather (1) to examine the reliability of some of the experimental data and methods used to obtain derived values for such constants, (2) to follow some of the recommended procedures which have proved useful in the appraisal of experimental data, and (3) to point out some of the apparent misinterpretations, inconsistencies, and discrepancies existing in the data on the properties of certain gases at pressures below 2 atmospheres.

II. AVAILABLE DATA

There are available in the literature very extensive data on the density or specific volume of different gases at various pressures and temperatures, often referred to as p,v,T data. Many of these published data are supposed to be the direct result of experiment and are frequently given in nonintegral multiples of some unit of density or specific volume, pressure, and temperature. Comparison of the experimental results of one observer with those of another observer, which are expressed in different nonintegral multiples of a different set of units, can be made accurately in general only by the expenditure of considerable arithmetical labor and by employing reliable methods of interpolation. Some data, which are given at integral temperatures and pressures, are supposed to be results obtained from experiments by some process of smoothing, the details of which are usually not specified. In some cases the results of a certain set of experiments, such as those obtained at a constant temperature, are given in the form of an empirical equation. In other cases a large group of experimental results covering a range of both temperature and pressure is embodied in a single equation, frequently called an equation of state. Many different forms of such equations with various degrees of complexity have been devised, but it is rather significant that there has been a pronounced decline in the number of such equations published in the last decade.

While it is possible to calculate from such equations not only the slopes of the pv isotherms but also many other important characteristics of gases, a serious difficulty arises if the demands as to accuracy are high and if careful consideration is given to the reliability of such derived results. In many instances the situation is so complex that it is exceedingly difficult, or next to impossible, to make even an educated guess as to the reliability of a derived result.

A superficial examination of the isothermal pv data discloses that the experimental results of the different observers in the range below 2 atmospheres generally differ markedly. Further investigation dis-

closes that the results derived from a given set of experiments, including observations above this range and also at about 1-atmosphere pressure, differ appreciably, depending upon the interpretation of the experimental data and the methods employed to obtain a derived result.

There appear to be two schools of thought relative to the best method of determining numerical values for the slopes of the *pv* isotherms below 2 atmospheres. One group of experimenters, working in the field of atomic and molecular weights, use only data obtained at and below 1-atmosphere pressure in the reduction of their data, completely ignoring the existence of data at higher pressures. The propriety of this procedure has been questioned by Wild [1].[1] In obtaining probable values for certain atomic weights and also the gas constant, Birge [2] identifies himself with this school by ignoring data above 1 atmosphere.

Another group of experimenters, working in the field of gas thermometry, make similar reductions of their results obtained at pressures below 2 atmospheres, but use values for the isothermal slopes deduced from pressures considerably above this range. The Physikalisch-Technische Reichsanstalt and the Leiden Cryogenic Laboratory have published extensive data obtained in the interval 1 to 100 atmospheres. Since the major use they have made of these data is in the reduction of their gas thermometry results, their position on the subject may be inferred.

Since both groups have one point in common, namely, at 1 atmosphere, which has been used almost universally as a conventional reference point, it appeared to be worth-while to examine the course of the *pv* curve on both sides of this reference point, using some of the most precise data obtained by each group. It is generally assumed by both groups that the *pv* versus p, or the *pv* versus $1/v$ curves are straight lines below 2 atmospheres within the experimental errors of the measurements. For the purpose of this paper, the slopes of these curves are regarded as important quantities whose numerical values are needed to the highest accuracy attainable for calculating other important derived physical constants.

III. THEORETICAL PREDICTIONS

While the approach here is chiefly from the experimental side, it may be well to summarize briefly some of the predictions of theory, especially those relating to the form of equation which may be expected to represent experimental results satisfactorily. One important prediction is that at 0° C, at least, no chemical changes such as dissociation and association are to be expected in the case of the simpler monatomic and diatomic gases. Another is that the pressure, p, is a function only of the density, ρ, of a given kind of gas at a fixed temperature. Suppose it is assumed that the function is a power series

$$p=a_0+a_1\rho+a_2\rho^2+a_3\rho^3+ \ . \ . \ . \ , \tag{3.1}$$

which is known to be capable of representing any curve if enough terms are employed. Suppose further that the constant coefficients, the a's, are determined from experimental data, using the method of

[1] Figures in brackets indicate the literature references at the end of this paper.

least squares. Theory demands that $a_0=0$, but it practically never turns out to be zero identically in a least-squares treatment of the experimental data. It is very generally agreed that this may easily be ascribed to experimental errors and that the series may be written

$$pv=\frac{p}{\rho}=a_1+a_2\rho+a_3\rho^2+ \ . \ . \ . \ , \tag{3.2}$$

where v is specific volume. It should be noted that pv has the physical dimensions of energy per unit mass, which makes it an important parameter from the standpoint of thermodynamics and statistical theory, which employ the well-known exact laws of conservation of mass and energy and permit the adding up of separate contributions to the total energy. Statistical theory predicts that at low pressures the foregoing series should be mathematically convergent, so that each succeeding term must be smaller than the preceding term.

All of these theoretical predictions appear to be amply supported by experiment. That the series is rapidly convergent is clearly indicated by the numerical values obtained from experiments which are considered later. For He, Ne, A, H_2, N_2 and O_2 at 0° C and one atmosphere, for example, the term $a_2\rho$ turns out to be less than 0.1 percent of a_1 in all cases, and the term $a_3\rho^2$ is at most of the order of a few parts in a million compared with a_1.

It is common practice to reduce pv measurements at pressures where high accuracy is attainable to low-pressure conditions in much the same way that accurate weighings are reduced to so-called vacuum conditions, that is, to what would have been obtained if the measurements had been made at very low pressures. The fact that accurate measurements cannot be made at low values of p and ρ appears in principle to be of no more practical importance than the fact that accurate weighings cannot be made in an absolute vacuum.

At very low pressures eq 3.2 reduces to a form which embodies the laws of ideal or perfect gases given in many textbooks, namely

$$pv=\frac{RT}{M}=a_1 \tag{3.3}$$

where v is the volume of 1 gram of gas, R is the universal gas constant, T is absolute temperature, and M is molecular weight, all three being determinable from combinations of experimental values for a_1.

Modern theories attribute the known deviations from the foregoing equation to the mutual interaction of the gaseous particles, sometimes referred to as Van der Waals' forces. It is generally agreed that the force of attraction between two such particles varies inversely as r^6, where r is the distance between centers. In some instances the force of repulsion is assumed to vary inversely as r^n, where n is about 9 to 12; in other instances an exponential relation is assumed. In any case, it seems clear that as the density is decreased indefinitely, the frequency of collisions, using the language of kinetic theory, must decrease. Since the average distance apart also decreases, the effects of Van der Waals' forces must also decrease, yielding values for a_1 at very low pressures which are independent of such effects, often called imperfections of the gases.

The situation at present, relative to the specific effects of such imperfections, appears to be that, while marked advances have been

made, the theory is not yet far enough advanced to predict sufficiently accurate values for the constant a_2 and that better experimental values are needed in order to test adequately various hypotheses, and to aid in the development of reliable theories.

IV. METHODS OF CALCULATION

An accurate value for a_2, which has a different value for every temperature, has been the major goal of many experimental investigations. Some of the methods used to calculate a_2 from a given set of measurements, particularly at higher pressures, are open to several serious objections, because these methods introduce inaccuracies in a_2 which appear to exceed the inaccuracies inherent in the measurements themselves. High accuracy in calculations of this kind, as in the measurements, can be obtained only by exercising eternal vigilance in a multiplicity of small details. Many of these details appear worthy of brief mention here, since they are frequently ignored by many workers in this field.

It seems to be generally agreed that least-squares methods yield the "best" results and at the same time furnish an impersonal method of calculating mathematical probable errors which may be attached to published data. There are in the present application what may be termed "chemical errors," introduced by the presence of impurities in the gases, and also "physical errors," introduced in the calibration of weights and of the instruments used to measure pressure in terms of the fundamental standards of mass, length, and time, as well as many other possible physical sources of error. The true probable error should include all three kinds of errors, but the chemical and physical errors generally cannot be evaluated adequately from published information. Only by comparison of results from several independent investigations which differ by more than the sum of their mathematical probable errors can evidence be obtained of the magnitude of the systematic errors.

Least-squares methods have been followed here, but as pointed out by Birge [2] some judgment must be used in particular applications. For example, many of the results from the atomic-weight group give densities at only three pressures. If three terms in eq 3.2 are used, the fit is exact. If only two terms are used and each measurement is given equal weight, the usual solution yields the best simultaneous set of values for a_1 and a_2 From the standpoint of atomic weights, the emphasis is on obtaining a_1, but the immediate emphasis here is on obtaining the best value of a_2 from the measurements.

Considerable arithmetical labor may be saved by choosing one point as a reference and eliminating a_1. While, in principle, any point might be chosen, 1 atmosphere and 0° C has been used for convenience and designated by the subscript zero throughout this paper, unless otherwise specifically stated. Thus, writing the equation for any corresponding values of p and ρ

$$pv = a_1 + a_2\rho$$

and for the reference point

$$p_0v_0 = a_1 + a_2\rho_0.$$

Elimination of a_1 gives

$$pv-p_0v_0=a_2\rho-a_2\rho_0 \text{ or } \frac{pv-p_0v_0}{\rho-\rho_0}=a_2.$$

The mean value of a_2 obtained by this method of calculation is the same as the one obtained by the previous method, if each point is again given equal weight.

Thus far no attention has been given to the question of dimensions and units. It is obvious that $a_2\rho$ must have the same dimensions as pv; hence the numerical value of a_2 depends upon the units used. The very large number of different units used to express p, v, and ρ make interconversions for different combinations of units very difficult and troublesome at times. Such difficulties may be easily eliminated by writing the equation in the equivalent forms

$$pv=p_0v_0\left[1+a_2'\left(\frac{\rho}{\rho_0}-1\right)\right] \text{ or } \frac{\dfrac{pv}{p_0v_0}-1}{\dfrac{\rho}{\rho_0}-1}=a_2',$$

in which a_2' is obviously dimensionless and independent of the units used for p, v, and ρ.

In many cases the density is not measured. The mass of gas is held constant and only the volume is measured, so that ρ/ρ_0 must be replaced by v_0/v. Similarly for convenience, ρ/ρ_0 is very frequently replaced by p/p_0, which involves an approximation good to better than 0.1 percent in most cases considered here below 2 atmospheres, which is better than a_2 is known in general. Another alteration sometimes made is the use of an exponential equation. Since $e^x=1+x+x^2/2+\cdots$, with $x=a_2'\ [(\rho/\rho_0)-1]$, which is here always less than 0.001 below 2 atmospheres, $x^2/2$ and higher-power terms are less than 1 in 10^6. None of the measurements of p or v appears to be reliable to better than this amount.

These several alterations are referred to later, so that the various forms are assembled here as

$$pv=p_0v_0\left[1+\alpha_1\left(\frac{v_0}{v}-1\right)\right] \text{ or } \frac{\dfrac{pv}{p_0v_0}-1}{\dfrac{v_0}{v}-1}=\alpha_1 \tag{4.1}$$

$$pv=p_0v_0e^{\alpha_2\left(\frac{v_0}{v}-1\right)} \qquad \text{or } \frac{\ln\dfrac{pv}{p_0v_0}}{\dfrac{v_0}{v}-1}=\alpha_2 \tag{4.2}$$

$$pv=p_0v_0\left[1+\alpha_3\left(\frac{p}{p_0}-1\right)\right] \text{or } \frac{\dfrac{pv}{p_0v_0}-1}{\dfrac{p}{p_0}-1}=\alpha_3 \tag{4.3}$$

$$pv=p_0v_0e^{\alpha_4\left(\frac{p}{p_0}-1\right)} \qquad \text{or } \frac{\ln\dfrac{pv}{p_0v_0}}{\dfrac{p}{p_0}-1}=\alpha_4. \tag{4.4}$$

The symbol α, with a different subscript for each form of equation, is used to denote that they are not identical in value, but for practical purposes the α's are all the same as a_2' in the range below 2 atmospheres. In precise language, each α represents a number obtained from measurements at any equilibrium state (pv) and at the reference state (p_0v_0) on a constant mass of gas at a constant temperature. In this sense the α's differ from the constant coefficient a_2 in that they are variable coefficients analogous to the α in the familiar equation $l=l_0[1+\alpha(t-t_0)]$, in which l is length, t is temperature, and α is usually called the coefficient of linear expansion. Over a short interval, all α's may be considered as constants for practical purposes, but measurements made over a wide interval prove them to be variables in every case. The fact that eq 4.1 to 4.4 all reduce to $0/0=\alpha$ at the reference state is of no consequence, for differentiation of these equations shows that all α's represent the derivative at this point, and hence they replace in the more exact mathematical language what have previously been called the isothermal pv slopes.

The analogy between the pv coefficients and the coefficient of linear expansion appears to be very close in several respects. For example, judgment dictates that, with the precision attainable, a highly reliable value for the coefficient of expansion of steel or fused silica cannot be obtained by making measurements at two temperatures 1 degree apart. The pv coefficients are correspondingly small and judgment again dictates that reliable values cannot be expected from measurements with attainable precision at pressures 1 atmosphere or less apart. In both cases it appears that greater reliability may be obtained by representing α, obtained from measurements over a wide interval, by means of an adequate empirical equation and then calculating therefrom a value of α at the reference point, which very probably would have been obtained if more precise measurements could have been made in the immediate vicinity of the reference point.

V. UNCERTAINTIES

The major objective here is to obtain not only a value for a_2 or α at 1 atmosphere from different investigations but also an estimate of reliability. In most investigations there are only a few, usually three to eight, essentially different points which serve to define a curve. The calculated value for the slope of the curve at 1 atmosphere may be so materially affected by systematic errors and by the form of analytical relation assumed to represent the curve that the calculated probable error may have but little significance as a criterion of reliability, and may give a false sense of security in the particular application. In order to make some allowance, although arbitrary, for such effects, the estimated uncertainty has been taken as approximately three times the mathematical probable error, following in general the recommendations of Rossini and Deming [3].

There are only two types of application used here. When α is assumed to be constant over an interval within the indicated precision of the data, the uncertainty, u, in the mean value of α is taken as

$$u=2\left[\frac{\Sigma w\Delta^2}{(n-1)(\Sigma w)}\right]^{\frac{1}{2}}. \tag{5.1}$$

When a linear relation such as $\alpha=a+bx$ is assumed, the uncertainty in a or the value of α when $x=0$, obtained by the method of least squares, is taken as

$$u=\frac{2}{(n-2)^{\frac{1}{2}}}\left[\frac{(\Sigma w\Delta^2)(\Sigma wx^2)}{(\Sigma wx)^2-(\Sigma w)(\Sigma wx^2)}\right]^{\frac{1}{2}}. \tag{5.2}$$

In both cases, n is the number of observations, w is the weight assigned, and Δ is the residual or difference between the observed and calculated value of α.

An estimate of the true but unknown uncertainty may be obtained by assigning errors to each element which enters into the final result. In most of the measurements it appears almost certain that the true errors in each element are less than 1 in 10^3. Hence, to an approximation good to better than 1 in 10^6, the error in pressure may be written

$$p'=p+\Delta p=p\left(1+\frac{\Delta p}{p}\right)=pe^{\frac{\Delta p}{p}}, \tag{5.3}$$

where p' is the true value, p is the observed value, Δp is the true error, and $\Delta p/p$ is the fractional error in p. Similar relations may be written for volume, v, mass, m; and temperature, T; so that

$$\frac{p'v'}{p_0'v_0'}=\frac{pv}{p_0v_0}e^{y}, \tag{5.4}$$

where the combined fractional errors are

$$y=\frac{\Delta p}{p}-\frac{\Delta p_0}{p_0}+\frac{\Delta v}{v}-\frac{\Delta v_0}{v_0}+\frac{\Delta m}{m}+\frac{\Delta T}{T}, \tag{5.5}$$

which includes possible errors in the assumed constancy of mass and temperature. Thus the true error in α appears in the last terms of relations, such as

$$\frac{\ln\frac{p'v'}{p_0'v_0'}}{\frac{p'}{p_0'}-1}=\frac{\ln\frac{pv}{p_0v_0}}{\frac{p}{p_0}-1}+\frac{y}{\frac{p}{p_0}-1} \quad \text{or} \quad \alpha_4'=\alpha_4+\frac{y}{\frac{p}{p_0}-1} \tag{5.6}$$

$$\frac{\frac{p'v'}{p_0'v_0'}-1}{\frac{p'}{p_0'}-1}=\frac{\frac{pv}{p_0v_0}-1}{\frac{p}{p_0}-1}+\frac{\frac{pv}{p_0v_0}y}{\frac{p}{p_0}-1}+\ \ldots \quad \text{or} \quad \alpha_3'=\alpha_3+\frac{\frac{pv}{p_0v_0}y}{\frac{p}{p_0}-1}+\ \ldots \tag{5.7}$$

and corresponding relations for α_1 and α_2 with $[(v_0/v)-1]$ in the denominator. The error in the denominator has been neglected for simplicity, since by hypothesis this affects α less than 1 in 10^3, while the last term may be many times this amount.

For oxygen and argon α is of the order of 10^{-3}. In order to obtain a value of α for oxygen or argon with a true uncertainty of less than 1

percent, the combined fractional errors, y, must be less than the following:

$\frac{p}{p_0}-1$	y
0.5	5×10^{-6}
1	10^{-5}
10	10^{-4}
100	10^{-3}

For the other gases included herein, α is about 4 to 6×10^{-4}, so that the corresponding requirements are only slightly higher.

The scatter of the computed values of α obtained from measurements at less than 2 atmospheres indicates random fractional errors of several units in 10^{-5}, even in the most precise measurements available, and very much larger errors in other cases, which it has not seemed worthwhile to consider in detail here. Since there is no positive assurance that the systematic errors may not be as large as or even larger than the apparent random errors, which already exceed the limits stated above, it is obvious that α cannot be obtained with a true uncertainty of less than 1 percent from available measurements at pressures less than 2 atmospheres.

With measurements over an interval of 10 atmospheres or more the requirements are obviously not so exacting. It appears that the combined fractional errors in some of the published measurements at high pressures may not exceed about 10^{-4} in several instances. One of the uncertainties in the values for α at 1 atmosphere obtained from measurements over a large pressure interval appears to be in the analytical relations used to represent α over such an interval. In several instances linear relations have been used, whereas the data clearly indicate that such a relation is inadequate. A constant error obviously introduces an erroneous apparent trend in the values of α. Hence, anomalous trends in the values of α may well be viewed with suspicion and interpreted as possible evidence of the presence of systematic errors. In some instances the variation of α with pressure is small, for example, a few units in 10^{-8} per atmosphere for helium. There appears to be little reason for doubting that the values of α for helium at 0° C and low pressures, obtained from measurements over a wide pressure interval, are much more reliable than the values obtained from any available measurements over a small pressure interval at low pressures.

In view of the fact that small errors of the order of 10^{-5} and less become significant in some instances, it may be pointed out that the method of calculation using ratios automatically eliminates the effect of some of the possible systematic errors of this magnitude. For example, where p and p_0 are both measured by means of a mercury manometer

$$\frac{p}{p_0}=\frac{\rho h g}{\rho_0 h_0 g}, \tag{5.8}$$

where ρ is the density of mercury, h is the height of mercury column, and g is the average gravitational acceleration at the place where p is measured. The absolute value of g is obviously eliminated, and the absolute values of density are not needed as long as the density is uniform and proper corrections for temperature and pressure are applied. Thus the uncertainty in the ratio p/p_0 reduces essentially to uncertainties in the measurements of h, except for capillary corrections

and other small but sometimes appreciable corrections, such as for gas columns.

The case is different, however, when p_0 is measured with a mercury manometer and p is measured with a piston gage. In this case

$$\frac{p}{p_0}=\frac{mg/A}{\rho_0 h_0 g}, \tag{5.9}$$

where A is the effective area of the piston and m is the effective mass of the piston and weights applied. The absolute value of g is eliminated, but uncertainties in the absolute values of all the other factors are involved. Thus an important element is the calibration of the piston gage, which is usually done by comparison with a mercury manometer; but many of the details of such calibrations are frequently not published. The agreement of results from different laboratories in several instances supplies indirect evidence that uncertainties in such calibrations apparently do not exceed about 10^{-4}.

Pressures much above 1 atmosphere are frequently determined at the Leiden Laboratory by means of closed-end manometers, which are usually filled with hydrogen. In Leiden Comm. 227a (1933) it is stated that in order to obtain a precision of 10^{-4} several improvements in the calibration and temperature control of the closed-end manometers were necessary. In a footnote, 1.35 mm is given as the radius of the tube containing the mercury meniscus. Uncertainties are recognized in the capillary corrections, which are relatively large in a tube of this size. There are also uncertainties in the volume of the gas beneath a plane tangent to the mercury surface, since the meniscus may assume various heights and shapes for a given setting of the vertex.

Illustrations are given later of other uncertainties which, for one reason or another, have found their way into some of the published values for α at low pressures. Many of the calculations of pv/p_0v_0 and α have been carried to one place beyond those given in the original publications, in order to obtain adequate values of u in equations 5.1 and 5.2 and to minimize uncertainties in the calculations themselves.

VI. OXYGEN

While the Reichsanstalt measurements include a number of gases and appear to be in reasonably good agreement with measurements obtained in other laboratories, all the analytical relations published as representations of the measurements appear to be somewhat erroneous. Since the reason for this unfortunate state of affairs is the same for all the gases and has not been pointed out previously, the data on oxygen are discussed in some detail as an illustration.

Referring to the data given in any horizontal row in table 1, the measurements were obtained essentially as follows: A pressure (column 1) is measured by means of a piston gage; a valve is closed, confining an unmeasured mass of gas in a known volume (column 2); another valve is opened, permitting the same mass of gas to expand into another known volume (column 4); and the pressure (column 3) is measured at approximately 1 atmosphere with a mercury manometer. The data in column 5, which were calculated from the data in the previous

four columns, were used by Holborn and Otto to derive the following equation:[2]

$$pv = 1.00130 - 1.30143 \times 10^{-3} p + 3.6898 \times 10^{-6} p^2, \qquad (6.1)$$

where p is in m Hg, and $v=1$ when $p=1$. This equation, transformed to the form used here with 0° C and 1 atmosphere as the reference state, becomes

$$\frac{pv}{p_0 v_0} = 1 - 98.451 \times 10^{-5}\left(\frac{p}{p_0} - 1\right) + 2.13056 \times 10^{-6}\left(\frac{p}{p_0} - 1\right)^2. \qquad (6.2)$$

[2] Attention is called to the fact that the values of c in the equations $pv = a + bp + cp^2$ for oxygen at 0°, 50°, and 100° C given in *Z. Physik* **10**, 371 (1922) are in error. Corrected values for c are given in a later summary, *Z. Physik* **33**, 6 (1925), which contains the equation quoted here.

TABLE 1.—*Data on oxygen at 0 °C and 1 to 100 atmospheres obtained by Holborn and Otto*

Columns 1, 2, 3, and 4, observed values quoted from Z. Physik **10**, 367 (1922).
Column 5, calculated from observed values.

Column 6, based on $\alpha = \frac{1}{v_0}\left(\frac{dpv}{dp}\right)_t = -9.5 \times 10^{-4}$.

Column 7, corrected to common reference state, $p_0 = 760$ mm Hg, from values in columns 5 and 6.
Column 8, values quoted from Handbuch der Experimental Physik, **8** pt. 2, p. 175, with 1 atmosphere as the reference state.
Column 9, obtained from data in column 1 by dividing by $p_0 = 760$ mm Hg.
Column 10, obtained by dividing data in column 9 by data in column 7.

p	v	p_0	v_0	Observed $\frac{pv}{p_0v_0}$	Correction to $p_0=760$	Corrected $\frac{pv}{p_0v_0}$	Corrected $\frac{pv}{p_0v_0}$	$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{10^4\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$	Mean values $-10^4\,\alpha_1$	$\frac{10^4\left(1-\frac{pv}{p_0v_0}\right)}{\frac{p}{p_0}-1}$	Mean values $-10^4\,\alpha_1$
1	2	3	4	5	6	7	8	9	10	11	12	13	14
mm Hg	*ml*	*mm Hg*	*ml*										
18960.1	106.025	775.06	2651.28	0.978268	-19×10^{-6}	0.978249	0.97798	24.9475	25.5022	8.8772		9.0828	
18995.0	106.024	776.63	2651.32	.978064	−21	.978043	.97778	24.9934	25.5545	8.9425	8.9415	9.1513	9.1506
19055.5	106.023	780.60	2646.83	.977836	−26	.977810	.97754	25.0735	25.6425	9.0048		9.2176	
37788.1	106.016	811.42	5157.09	.957362	−64	.957298	.95706	49.7212	51.9392	8.3829	8.3858	8.7646	8.7680
37811.0	106.015	813.90	5144.74	.957306	−67	.957239	.95701	49.7513	51.9737	8.3888		8.7713	
56045.1	106.005	766.73	8246.73	.939593	−8	.939585	.93930	73.7436	78.4853	7.7970	7.7670	8.3053	8.2892
56098.2	106.006	766.79	8252.82	.939725	−9	.939716	.93943	73.8134	78.5486	7.7371		8.2729	
74849.0	105.998	798.74	10741.62	.924716	−48	.924668	.92442	98.4855	106.5090	7.1399	7.1331	7.7275	7.7220
75394.8	105.998	804.99	10741.04	.924277	−56	.924221	.92398	99.2037	107.3376	7.1263		7.7165	

In figure 1 the coordinates of the points for oxygen on curves 2 and 3 are:
2 3 3 2

Equation 6.1 was apparently derived so as to reduce to $pv=1$ when $p=1$ m Hg, but the data in column 5 are obviously not on this basis. As a matter of fact, each row of data in the first five columns applies to a particular mass of gas and the different rows are not on a comparable basis. Adding to the data in column 5 the corrections in column 6 yields the data in column 7, which are all on the same basis. The corrections are relatively small, since p_0 observed is not far from 760 mm. In other instances, p_0 observed ranged from less than 500 mm to over 900 mm, and the corrections are larger. Applications of these necessary corrections materially improve the general consistency of the Reichsanstalt measurements.

Holborn and Otto have evidently misinterpreted all their measurements as having 1 m Hg and 0° C, as the reference state, possibly

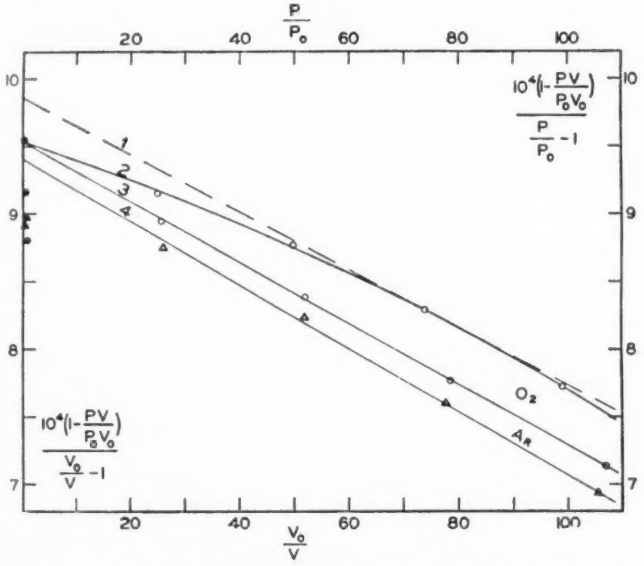

FIGURE 1.—*Data on oxygen (circles) and argon (triangles) at 0° C; Reichsanstalt data at 25 to 100 atmospheres; Baxter and Starkweather data below 1 atmosphere.*

Coordinates of lines 1 and 2 at top and right; coordinates of lines 3 and 4 at bottom and left. Line 1 represents eq 6.2; line 2 represents α_3 as a quadratic function of p/p_0. Line 3 represents eq 6.3 for oxygen. Line 4 represents eq 7.1 for argon.

because p in m Hg was used for convenience in the equations. Further evidence of this misinterpretation is supplied by the values in column 8, which are given by Otto in the Handbuch der Experimental Physik. Apparently these values were obtained from column 5, misinterpreted as on a 1 m Hg basis, and corrected to a 760 mm Hg basis. The effect of this misinterpretation is shown graphically in figure 1. The dashed line 1 at the top, representing eq 6.2, is obviously a very poor representation of the observed points and consequently yields an erroneous value of α at 1 atmosphere.

Curve 2 in figure 1 indicates clearly that the observed values of α_3 given in table 1 cannot be represented adequately by a straight line. On the other hand, line 3 indicates that it represents reasonably

well the observed values of α_1 in table 1. The weighted least-squares equation for line 3 is

$$\frac{pv}{p_0v_0}=1-(95.13\pm0.94)\times10^{-5}\left(\frac{v_0}{v}-1\right)+2.246\times10^{-6}\left(\frac{v_0}{v}-1\right)^2. \quad (6.3)$$

The values of α_1 obtained from measurements below 1 atmosphere by Baxter and Starkweather, considered later, have been included in figure 1 to indicate that they appear inconsistent with the Reichsanstalt measurements, as might be expected from the previous discussion on uncertainties.

Measurements on oxygen obtained at the Leiden Laboratory are quoted in table 2. The values of α_1 in column 4 are insufficient to give an adequate determination of the variation of α_1 with density, which has been assumed in column 5 from eq 6.3. The mean value of α_1 at 1 atmosphere (column 6) is in good agreement with the value obtained from the Reichsanstalt measurements, eq 6.3.

TABLE 2.—*Data on oxygen at 0° C and 1 to 55 atmospheres obtained by Van Urk and Nijhoff*

[Columns 1, 2, and 3 quoted from Leiden Comm., 169c (1924). H. A. Kuypers and H. K. Onnes, Leiden Comm. 165a (1923) give for oxygen at 0° C the equation $pv/p_0v_0=1.00095-95.803\times10^{-5}\ (v_0/v)+2.0606\times10^{-6}(v_0/v)^2$ expressed in the symbols used here.]

$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{pv}{p_0v_0}$	$\frac{10^5\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$	$0.2246\left(\frac{v_0}{v}-1\right)$	$-10^5\alpha_1$ at $\frac{v_0}{v}=1$
1	2	3	4	5	6
36.20	37.38	0.9685	86.6	8.1	94.7
38.77	40.13	.9661	86.7	8.8	95.5
46.90	48.91	.9590	85.6	10.8	96.4
47.15	49.17	.9589	85.4	10.8	96.2
54.75	57.45	.9528	83.6	12.7	96.3
				Mean	95.8

VII. ARGON

The Reichsanstalt measurements on argon are quoted in table 3, and values of α_1 are plotted in figure 1. It is apparent from line 4 that α_1 for argon is very similar to α_1 for oxygen (line 3). The equation for line 4, obtained graphically,[3] is

$$\frac{pv}{p_0v_0}=1-93.90\times10^{-5}\left(\frac{v_0}{v}-1\right)+0.235\times10^{-5}\left(\frac{v_0}{v}-1\right)^2, \quad (7.1)$$

which yields $10^5\alpha=-93.9$ at 0° C and 1 atmosphere. The equation, given by Holborn and Otto [4] based on the same data, yields $10^5\alpha=-98.1$ at 1 atmosphere. The difference, about 4 percent, is about the same as that previously found for oxygen, and for the same reason.

[3] Least-squares methods were not used in this case because the corrections to $p_0=760$ could not be applied, the details of the measurements not being given by Holborn and Schultze. The results (see fig. 1) parallel those for oxygen so closely that $10^5\alpha=-94\pm1$ at 1 atmosphere was taken as a reasonable estimate from a large-scale plot.

TABLE 3.—*Data on argon at 0° C and 1 to 100 atmospheres obtained by Holborn and Schultze*

[Columns 1 and 2 quoted from Ann. Physik **47**, 1089 (1915). The details of the measurements, such as quoted for oxygen, are not given. It is assumed here that the reference pressures, p_0, were sufficiently close to 760 mm Hg that corrections would amount to less than 1 in $10^5\ \alpha_1$. See notes on the measurements of Holborn and Schultze on helium for evidence in support of this assumption.]

p	$\frac{pv}{p_0v_0}$	$\frac{10^5\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$	$0.235\left(\frac{v_0}{v}-1\right)$	$-10^5\,\alpha_1$ at $_{v_0=1}\alpha$
1	2	3	4	5
*m*Hg				
19.230	0.97826	87.43	5.84	93.27
19.258	.97821	87.50	5.85	93.35
37.552	.95817	82.72	11.93	94.65
37.940	.95809	82.01	12.03	94.04
55.521	.94192	76.00	17.96	93.96
55.611	.94173	75.97	18.02	93.99
74.395	.92746	69.39	24.57	94.01
74.408	.92746	69.38	24.58	93.95
			Mean.....	93.90

Measurements obtained on argon at the Leiden Laboratory are quoted in the first part of table 4. The values of $10^5\ \alpha_1$, ranging from -72 to -75, were not plotted in figure 1 because they are grossly inconsistent with the Reichsanstalt data, as pointed out by Holborn and Schultze. A plausible clue to the reason for the large discrepancy is given by Wild [1] in a footnote, quoted as follows: "Professor Masson, of the University of Durham, informs me that Onnes' data on argon are in error, due to 'side trapping' of a small amount of gas in one limb of the piezometer, after measurement of its volume at one atmosphere."

By choosing one of the high-pressure measurements as the reference state and eliminating v_0 at 1 atmosphere, it may readily be shown that the data at 1 atmosphere are not consistent with the data at the higher pressures. The value of v_0 obtained by this process is greater by the factor 1.0035. The calculations made on this basis in the second part of table 4 lead to a value of $10^5\ \alpha = -93$ at 1 atmosphere, which is in fair agreement with that obtained from the Reichsanstalt measurements.

Attention is called to the fact that Onnes and Crommelin reported data for argon on 16 different isotherms, which are quoted in International Critical Tables, volume 3, page 4. All the data are based upon what appears to be an erroneous value for v_0.

TABLE 4.—*Data on argon at 0° C and 1 to 62 atmospheres obtained by Onnes and Crommelin*

Columns 1, 2, and 3 quoted from *Leiden Comm.* 118b (1910).
Column 4. These values of α_1 are inadequate to establish the change of α_1 with density.
Column 5. The value of 0.235 was assumed from the Reichsanstalt data on argon, eq 7.1, since the data in column 4 are insufficient to yield an adequate value for the change of α_1 with density.

$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{pv}{p_0v_0}$	$\frac{10^5\left(1-\frac{pv}{p_0v_0}\right)}{\frac{v_0}{v}-1}$	$0.235\left(\frac{v_0}{v}-1\right)$	$-10^5\,\alpha_1$ at $\frac{v_0}{v}=1$
1	2	3	4	5	6
20.576	20.877	0.98560	72.4	.....	.....
26.070	26.581	.98077	75.2	.....	.....
31.572	32.302	.97740	72.2	.....	.....
36.743	37.782	.97250	74.8	.....	.....
49.871	51.840	.96201	74.7	.....	.....
62.230	65.325	.95261	73.7	.....	.....
(REFERENCE VOLUME, v_0, INCREASED BY THE FACTOR 1.0035)					
20.576	20.950	0.98215	89.5	4.7	94.2
26.070	26.674	.97736	88.2	6.0	94.2
31.572	32.415	.97399	82.8	7.4	90.2
36.743	37.914	.96911	83.7	8.7	92.4
49.871	52.021	.95867	81.0	12.0	93.0
62.230	65.554	.94929	78.6	15.2	93.8
				Mean.....	93.0

VIII. HYDROGEN

In the measurements at the Reichsanstalt and also the Leiden Laboratory, large corrections are required, since large portions of the gas were at about room temperature instead of the particular isotherm under investigation. In the measurements at the Van der Waals Laboratory of the University of Amsterdam by Michels and collaborators, there are no such corrections, since all the gas was at the same temperature, confined over mercury in a glass piezometer shaped somewhat like a McLeod gage, with a large lower bulb for determinations of v_0 at 1 atmosphere and a series of small upper bulbs with electric contacts sealed into the capillaries between the small bulbs. With the same pressure inside and outside the glass piezometer, the measurements were carried to much higher pressures. The precision of the measurements is much higher than in any other measurements available. The measurements obtained on hydrogen are quoted in table 5. With only six measurements of pv/p_0v_0, these were represented by a power series with five coefficients, only the first three coefficients being given in the publication cited, which yield $10^5\alpha=61.16$ at 0° C and 1 atmosphere. The reliability of this value is difficult to estimate under the circumstances.

Considerable effort has been devoted here to finding simple, yet adequate, interpolation equations in order that the advantages of least-squares methods may be fully utilized without undue labor, and as an aid in obtaining impersonal estimates of uncertainties in α at low pressures. Many people, including the author, rebel at using least-squares methods when more than about two unknown coefficients are involved, and especially when the number of observations approaches the number of unknown coefficients.

As an illustration of the characteristics of the four different α's defined by eq 4.1 to 4.4, calculated values over a wide interval are given in table 5 and are plotted as open circles in figure 2, the numbers 1 to 4 on the curves corresponding to α_1, α_2, α_3 and α_4 respectively. For curves 1 and 2, the abscissas are v_0/v, and for curves 3 and 4, the abscissas are p/p_0. Obviously, curves 1, 3, and 5 cannot be represented adequately by a linear equation; even a quadratic equa-

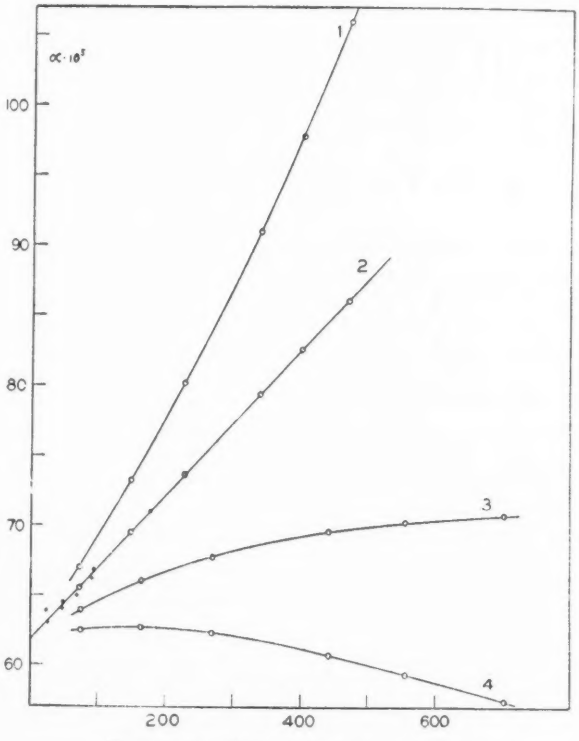

FIGURE 2.—*Data on hydrogen at 0° C.*

Curves 1, 2, 3, and 4 represent α_1, α_2, α_3, and α_4, respectively, calculated in table 5 from data of Michels, Nijhoff, and Gerber (open circles).
The abscissas for curves 1 and 2 are v_0/v; for curves 3 and 4 the abscissas are p/p_0. The data of Holborn are represented by crosses; data of Wiebe and Gaddy are represented by closed circles.

tion is insufficient. Curve 2 is apparently linear within the precision of the data and the equal weight, least-squares equation is

$$10^5 \ln \frac{pv}{p_0 v_0} = (61.869 \pm 0.073)\left(\frac{v_0}{v} - 1\right) + 0.05175\left(\frac{v_0}{v} - 1\right)^2. \quad (8.1)$$

On a large-scale drawing, using a straightedge for curve 2 and a celluloid spline, held in place by lead weights for drawing curves 1, 3, and 4, it was apparent that all four curves tended to approach smoothly the same value of α at 1 atmosphere to about three significant figures.

TABLE 5.—*Data on hydrogen at 0° C and 1 to 700 atmospheres obtained by Michels, Nijhoff, and Gerber*

Columns 1 and 2 quoted from *Ann. physik* **12**, 562 (1932). Values in other columns were computed from these experimental values.

$\frac{p}{p_0}$ (1)	$\frac{v_0}{v}$ (2)	$\frac{pv}{p_0v_0}$ (3)	$\frac{10^5\left(\frac{pv}{p_0v_0}-1\right)}{\frac{v_0}{v}-1}$ $10^5\,\alpha_1$	$\frac{10^5 \ln \frac{pv}{p_0v_0}}{\frac{v_0}{v}-1}$ $10^5\,\alpha_2$	$\frac{10^5\left(\frac{pv}{p_0v_0}-1\right)}{\frac{p}{p_0}-1}$ $10^5\,\alpha_3$	$\frac{10^5 \ln \frac{pv}{p_0v_0}}{\frac{p}{p_0}-1}$ $10^5\,\alpha_4$
75.795	72.334	1.04785	67.08	65.51	63.97	62.48
164.193	148.221	1.10776	73.196	69.515	66.032	62.711
268.99	227.641	1.18164	80.144	73.642	67.779	62.278
442.27	338.39	1.30698	90.987	79.350	69.569	60.670
556.89	400.47	1.39059	97.777	82.541	70.264	59.315
701.34	468.89	1.49575	105.954	86.052	70.787	57.490

In figure 2 the coordinates of the points on the four curves are as follows:

3 and 4	1 and 2	1	2	3	4

The measurements of other observers on hydrogen are not given in detail here in order to conserve space. For purposes of comparison, values for α_2 from two other laboratories are also shown in figure 2. Mean values at about 25, 50, 75, and 100 atmospheres obtained from 11 measurements reported by Holborn [5], when corrected, as previously indicated for oxygen and when the slope of line 2, figure 2, is assumed to be that given by the last coefficient in eq 8.1, lead to an equal weight, mean value of $10^5\,\alpha=61.6\pm0.3$ at 1 atmosphere, while the equation given by Holborn gives $10^5\,\alpha=62.4$. The four measurements reported by Wiebe and Gaddy[6] at 25, 50, 100, and 200 atmospheres, yield an equal weight, mean value of $10^5\,\alpha=62.0\pm0.3$ at 1 atmosphere, when the slope of line 2, figure 2, is assumed as stated above.

The agreement of three values at 1 atmosphere for $10^5\,\alpha$, namely 61.87 ± 0.07, 61.6 ± 0.3, and 62.0 ± 0.3, obtained from measurements in three different laboratories is very gratifying and very significant, if it is interpreted as evidence that systematic errors in measurements made in these laboratories were small. The foregoing values are consistent with the extensive measurements on hydrogen at 20° C made at the Leiden Laboratory with a multiple-column, open-end, mercury manometer by Schalkwijk [7], when α_2 is calculated and compared with the measurements indicated by line 2, figure 2. The measurements reported by Nijhoff and Keesom [8] at 0° C, made with a closed-end mercury manometer, are less precise and lead to a value for α at 1 atmosphere, which is lower than those given above by a few percent.

IX. NITROGEN

Measurements on nitrogen obtained at the Van der Waals Laboratory of the University of Amsterdam are quoted in table 6. Michels, Wouters, and De Boer state that "series evaluation * * * carried out according to the method of mean squares" yielded the following equations:

$$10^5\frac{pv}{p_0v_0}=100045-46.020\frac{p}{p_0}+0.30048\left(\frac{p}{p_0}\right)^2-1.35\times10^{-7}\left(\frac{p}{p_0}\right)^4 \quad (9.1)$$

$$10^5\frac{pv}{p_0v_0}=100045-45.860\frac{v_0}{v}+0.30643\left(\frac{v_0}{v}\right)^2-1.84\times10^{-6}\left(\frac{v_0}{v}\right)^4, \quad (9.2)$$

which were obtained from their paper but are expressed in the symbols used here.

In order to test the effect on α at 1 atmosphere when a different form of equation was used and also to obtain an estimate of uncertainty, the following least-squares equation

$$10^5 \ln\frac{pv}{p_0v_0}=(-45.3166\pm0.308)\left(\frac{v_0}{v}-1\right)+0.29868\left(\frac{v_0}{v}-1\right)^2 \quad (9.3)$$

was obtained from the same data, weighting each observation proportionally to $[(v_0/v)-1]$. As a check, the calculations were repeated, giving each observation equal weight, which yielded

$$10^5 \ln\frac{pv}{p_0v_0}=(-45.3236\pm0.352)\left(\frac{v_0}{v}-1\right)+0.29885\left(\frac{v_0}{v}-1\right)^2. \quad (9.4)$$

TABLE 6.—*Data on nitrogen at 0° C and 1 to 52 atmospheres obtained by Michels, Wouters, and De Boer*

Columns 1, 2, 3, 4, and 5 quoted from Physica **1**, 587 (1934)

$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{pv}{p_0v_0}$	10^5 (observed-calculated)			
			Equation 9.1	Equation 9.2	Equation 9.3	Equation 9.4
1	2	3	4	5	6	7
19.0215	19.1606	0.99274	−4	−5	−4	−4
23.7629	23.9734	.99122	1	1	1	2
28.4968	28.7894	.98983	6	6	6	7
33.1101	33.4951	.98851	1	1	1	2
37.9526	38.4409	.98730	−1	−1	0	0
42.7435	43.3413	.98621	−6	−6	−5	−5
47.4376	48.1401	.98541	4	3	3	3
52.2160	53.0328	.98460	0	0	−3	−3

A comparison of the four equations is given in table 6, where the deviations of eq 9.1 and 9.2 have been copied from table 2 of the paper by Michels, Wouters, and De Boer. There is obviously very little difference between the various equations as far as representing the measurements is concerned, but there is considerable difference in the labor required to obtain four unknown coefficients in eq 9.1 and 9.2 and only two coefficients in 9.3 and 9.4 which were calculated with the equation in the linear form

$$\alpha_2=A+Bx \text{ or } \frac{\ln\frac{pv}{p_0v_0}}{\frac{v_0}{v}-1}=A+B\left(\frac{v_0}{v}-1\right). \quad (9.5)$$

Furthermore, calculation of the uncertainty in α at 1 atmosphere from equations such as 9.1 and 9.2 is complicated, while such a calcu-

lation is simple with eq 9.5. Differentiation of each equation gives for α at 1 atmosphere

$-10^5\alpha$	Equation
45.42	9.1
45.25	9.2
45.32±0.31 [4]	9.3
45.32±0.35 [4]	9.4

Michels, Wouters, and De Boer give some discussion of uncertainties in their measurements. The total volume, v_0, of the piezometer is given as about 1,500 cm^3, which means that the actual volumes of the gas at 0° C and 19 to 52 atmospheres were between about 75 to 30 cm^3.

In a joint publication from the Reichsanstalt and the University of Amsterdam, Otto, Michels, and Wouters [9] report measurements on nitrogen at 0° C and 45 to 227 atmospheres, in which the volume, v_0, of the piezometer is stated to be about 98 cm^3 and the volumes at high pressure to be between 2 and 0.43 cm^3. With nine different measurements of pv/p_0v_0, these authors represent their results at 0° C by means of two equations similar in form to eq 9.1 and 9.2 but with two more coefficients for sixth- and eighth-power terms, making a total of six coefficients. The authors do not state that the method of least squares was used in obtaining their equations, which, upon differentiation, yield two values for $-10^5\ \alpha$ at 1 atmosphere, namely, 45.31 and 44.70, corresponding to equations similar to eq 9.1 and 9.2, respectively.

Uncertainties in these two values are difficult to estimate under the circumstances, but it seems safe to infer from the evidence available that the true uncertainty in any value of α at 1 atmosphere, obtained from the same measurements by any accurate method of calculation, would exceed the true uncertainty in the value of α obtained from the measurements quoted in table 6. In other words, the values of α at 1 atmosphere obtained from the two investigations may be said to be in agreement, or at least not in conflict, within reasonable estimates of uncertainties. Apparently the same statement might be applied to the values of α for nitrogen at 0° C and 1 atmosphere obtained from many other investigations, some of which are listed by Otto, Michels, and Wouters [9], while Keesom and Tuyn [10] [5] list from 15 different sources values of $-10^5\ \alpha$, which range from 37.2 (credited to Amagat) to 54.1 (credited to Bartlett).

No attempt can be made here to give an adequate discussion of calculations of the slopes of isotherms other than 0° C, but it may be of interest to outline briefly a possible procedure in examining the reliability of data available on nitrogen at 100° C. Suppose an equation similar to eq 9.4, but written in the more general form

$$\ln \frac{pv}{p_0v_0} = A + B\frac{v_0}{v} + C\left(\frac{v_0}{v}\right)^2 + \ldots\ , \tag{9.6}$$

[4] See eq 5.2 for the interpretation of $\pm u$, as used here. Readers accustomed to thinking in terms of least-squares probable error should mentally divide $\pm u$ by 3.

[5] This reference may be consulted for an extensive bibliography of p,v,T data on He, H_2, and N_2.

is assumed for the 100° C. isotherm, and that the coefficients A, B, and C are determined by least-squares methods, using the data given by Michels, Wouters, and De Boer, which include eight values [6] of pv/p_0v_0 at 100° C. for the same values of v_0/v quoted in table 6. Subtracting two such equations, one for 100° C. and one for 0° C., already obtained, yields

$$\ln \frac{(pv)_{100°}}{(pv)_{0°}} = (A_{100} - A_0) + (B_{100} - B_0)\frac{v_0}{v} + (C_{100} - C_0)\left(\frac{v_0}{v}\right)^2 + \ldots . \quad (9.7)$$

It so happens that for nitrogen, C_{100} is very nearly equal to C_0, so that at constant volume $\ln p_{100°}/p_{0°}$ is very nearly linear in v_0/v over the range covered. Visual evidence of this is given in figure 3, where a linear scale of logarithms is used for the ordinates. The three points near the ordinate axis were obtained from the constant-volume gas-thermometer measurements of Beattie [11]. While measurements are reported at five different pressures, two intermediate points are not shown, for clarity. The other eight points were obtained from the essentially constant-volume gas-thermometer measurements of Michels, Wouters, and De Boer, and the line was drawn with a straightedge. The data from the two investigations appear to be mutually consistent to a few parts in 10^5, and consistent with an intersection with the ordinate axis between 1.3660 and 1.3661 on a large-scale plot.

It may be noted that

$$\ln \frac{(pv)_{100°}}{(pv)_{0°}} \doteq \ln \frac{T_{100}}{T_0} \doteq A_{100} - A_0 \text{ as } \frac{v_0}{v} \doteq 0$$

and

$$T_0 = \frac{100}{\frac{T_{100}}{T_0} - 1},$$

by definition; hence

$$T_0 = \frac{100}{e^{(A_{100} - A_0)} - 1} .$$

Thus a value for T_0, the ice point on the thermodynamic scale, may be obtained from the measurements of Michels, Wouters, and De Boer, but the calculated uncertainty in T_0 would obviously turn out to be relatively large.

A value of T_0 has been calculated by Beattie [11] based entirely on his measurements with nitrogen. He has also calculated values of T_0, using in principle three different values for the rate of change of $p_{100°}/p_{0°}$ obtained by various roundabout processes from measurements of Joule-Thomson coefficients, or of pv/p_0v_0 at higher pressures, which make the calculation of uncertainties very complicated. A more direct method of calculation of T_0 from the data on nitrogen appears

[6] In obtaining the values of pv/p_0v_0 at 100° C., corrections were applied by Michels, Wouters, and De Boer for changes in volume of the glass piezometer with temperature and pressure, and for the fact that the temperature actually observed was 99.720° C. instead of 100° C. No mention is made of a correction for the vapor pressure of mercury, which is known to be about 0.0004 atmosphere at 100° C. The effect of such a correction if not already applied, would be to lower slightly the points shown in figure 3, a perceptible amount at $v_0/v = 19$ on a large-scale plot, and barely perceptibly at $v_0/v = 52$.

to be to combine the two sets of data shown in figure 3, using the observed ratios $p_{100°}/p_{0°}$. This may be done in several different ways.

One method is to use an adequate form of equation, preferably with a minimum of unknown coefficients, and a judicious assignment of weights to each observation. This method gives the high-pressure data the weight to which they appear entitled. Another method, which seems to lead to essentially the same final result and is sometimes preferable, because it is simpler, is to combine the data at low and high pressures to obtain a value for the rate of change of $p_{100°}/p_{0°}$ with either p/p_0 or v_0/v and to use this value to reduce each individual observed ratio $p_{100°}/p_{0°}$ near the ordinate axis and thus obtained a weighted mean value for $p_{100°}/p_{0°}=T_{100}/T_0$. In spite of the apparent advantages

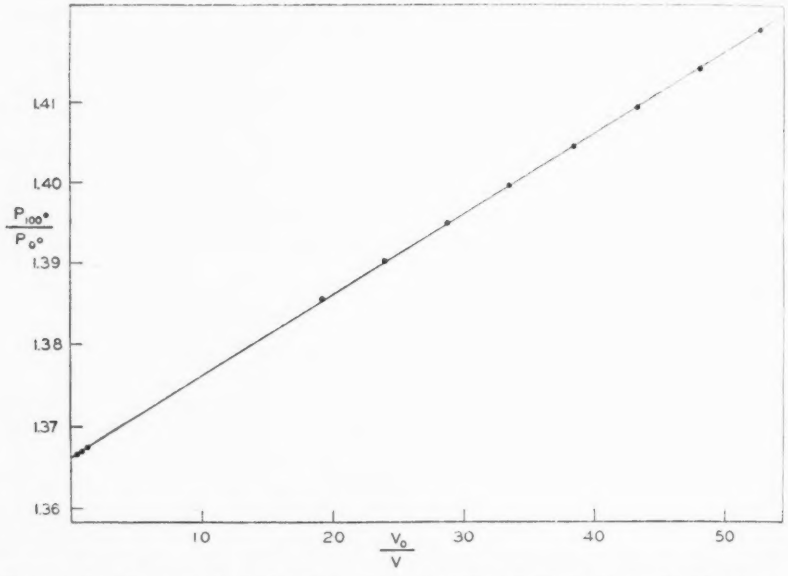

FIGURE 3.—*Data on the ratio of pressures at 100° and 0° C, obtained with nitrogen at constant volume by Beattie below 2 atmospheres, and by Michels, Wouters, and De Boer at 19 to 52 atmospheres.*

of these two methods of calculation, neither of them has ever been used to calculate T_0 or the uncertainty in T_0.

In this connection, it may be noted that the rate of change of $p_{100°}/p_{0°}$ at low pressures may be calculated from the measurements of Beattie alone, or it may be calculated by using only the measurements of Michels, Wouter, and De Boer and a method similar to the one outlined above. When consideration is given to the possible effects of constant or systematic errors in each investigation, it seems probable that a combination of both sets of data should yield a more reliable value for the rate of change of $p_{100°}/p_{0°}$, which is larger and hence of more importance for nitrogen than for some of the other thermometric gases. The result of such a combination leads to a relative value for the slopes at low pressures of the pv isotherms at 0 and 100 °C, or for practical purposes a value for $B_{100} - B_0$ in eq 9.7 or similar equations, and the uncertainty in the value for this difference may be calculated.

It is emphasized that this procedure seems preferable to the one usually followed, namely to obtain values for B_{100} and B_0 from the data on each isotherm separately, and then to obtain the difference. A value for $B_{100} - B_0$ may be calculated from measurements of the Joule-Thomson coefficient and the specific heat at constant pressure, but calculations of uncertainties are very complex, in fact impossible, since most of the primary Joule-Thomson data are reported in graphical form only. Apparently there are no Joule-Thomson measurements below 1 atmosphere pressure. Short extrapolations of pv data at constant volume or constant pressue appear to introduce no greater uncertainties in calculations of T_0 than the necessary extrapolations of Joule-Thomson data in order to apply them to gas-thermometer data at pressures below 1 atmosphere.

Another method of calculation, namely, a method of successive approximations, which may be used to advantage in the special case[7] when the data are given at constant volume or density, is to use eq 9.6 or 9.7 or an equivalent equation in the form

$$\ln\frac{(pv)_t}{(pv)_0^\circ}=\ln\frac{T}{T_0}+(B_t-B_0)\frac{v_0}{v}+(C_t-C_0)\left(\frac{v_0}{v}\right)^2+\ \ldots\ ., \qquad (9.8)$$

where $v_t=v0^\circ$ and v_0 is the reference volume at 0° C and 1 atmosphere. A value for T_0 may be assumed and any error in t° C, observed or reported, may be neglected for the first approximation, yielding a value for $T/T_0=1+t/T_0$. Values for (B_t-B_0) and (C_t-C_0) may be obtained from data on p_t/p_0° at the higher pressures by graphical or least-squares methods, and these values used to correct low-pressure constant-volume gas-thermometer measurements to obtain a better value for T/T_0; and the process may be repeated, if necessary. The calculations may be made conveniently with eq 9.8 in the form

$$y=\frac{v}{v_0}\ln\frac{p_t}{p0^\circ}\,\frac{T_0}{T}=(B_t-B_0)+(C_t-C_0)\frac{v_0}{v}+\ \ldots\ ., \qquad (9.9)$$

since calculated values of y usually do not vary much over a moderate range of v_0/v. Values of y may be plotted on a sufficiently open scale to determine how many terms to use or to inspect the data for evidence of anomalous trends. Such trends may be caused by systematic

[7] In the more general case, when the values of pv/p_0v_0 at 0° C and on the isotherm, T, are not given at constant volume or density and gas-thermometer data at low pressures are lacking, the following procedure may be used for a first approximation. In addition to assuming a value for T/T_0, a value at 0° C and $v_0/v=0$ may be assumed for $pv/p_0v_0=RT_0/p_0v_0$, designated by $1+\lambda$ in International Critical Tables, vol. 3. Each individual value for pv/p_0v_0 on any isotherm, T, may then be converted to

$$\frac{pv}{p_0v_0}\cdot\frac{p_0v_0}{RT_0}\cdot\frac{T_0}{T}=\frac{pv}{RT}.$$

Equation 9.6 may then be written in the form

$$\ln\frac{pv}{RT}=B\frac{v_0}{v}+C\left(\frac{v_0}{v}\right)^2+\ \ldots\ .$$

or better still in the form

$$\alpha_0=\frac{v}{v_0}\ln\frac{pv}{RT}=B+C\frac{v_0}{v}+\ \ldots\ .$$

Thus values for α_0 may be plotted against v_0/v and approximate values for B and C may be obtained easily. A method similar to this has been applied to data on CO_2 over a wide range of pressures and in the critical region by the Demings, *Phys. Rev.* **56**, 108 (1939).

errors in the assumed values for T_0 and $t°$ C or elsewhere [8] in the measurements of pv/p_0v_0.

In applying this method of calculation to the particular case of the eight pairs of values of pv/p_0v_0 given by Michels, Wouters, and De Boer, each pair of values are at constant volume, giving one value for $p_{100°}/p_{0°}$ used in plotting figure 3. It may be noted that by assuming $T_0=273.16\pm0.02$ and neglecting any error in the reported values for $t=0$ °C and $t=100$ °C, gives $T_{100}/T_0=1.36609\pm0.00003$ as a point on the ordinate axis of figure 3, which may be used in the calculations to replace, in effect, the low-density gas-thermometer measurements of Beattie or of other observers. The true uncertainty in this value is probably less than the true uncertainty in any of the values of $p_{100°}/p_{0°}$ at higher densities. If the curve or the equation for the curve is not restricted at low densities, such as in least-squares calculations, using eq 9.7 and the eight higher points above, small errors, especially in the lower one or two points, may be so magnified as to lead to an intersection with the ordinate axis at 1.3663, which is far outside the limits of uncertainty assumed above, and the value for the slope of the curve at low densities, essentially $B_{100}-B_0$, is likewise more uncertain than when the equation for the curve is restricted at $v_0/v=0$.

A reliable value for the ratio T/T_0 is the goal sought in most measurements with a constant-volume gas thermometer. Several different tables of corrections to be applied to measurements made at different temperatures with nitrogen or other gases with different ice-point pressures have been published. Values for such corrections are obviously a great convenience in gas-thermometer calculations, but the reliability of some of the published values may be questioned, since many of the corrections depend upon values for $B_{100}-B_0$ and B_t-B_0 calculated from data on pv/p_0v_0 at high pressures on each isotherm separately, without restriction at low pressures in some instances, with $T_0=273.09$ or $T_0=273.20$ in other instances, and with many other uncertainties involved, some of which are mentioned in other sections of this paper.

X. HELIUM

Measurements on helium at 0 °C and up to 1,000 atmospheres obtained by Wiebe, Gaddy, and Heins are quoted in table 7. These authors reported the following least-squares equation:

$$\frac{pv}{p_0v_0}=1.00059+52.17\times10^{-5}\frac{p}{p_0}-3.876\times10^{-5}\left(\frac{p}{p_0}\right)^2. \qquad (10.1)$$

This equation is an illustration of many to be found in the literature that fail to represent the reference state of the gas, which should be taken as exact for purposes of calculation. It was mentioned previously, and is emphasized again, that the measurement of the volume, v_0, of the gas at 0 °C and 1 atmosphere takes the place of a measurement of the mass of the gas, so that v_0/v is, in a sense, a density, sometimes called Amagat density. Obviously, eq 10.1 and the

[8] The data at 0° and 100° C given by Michels, Wouters, and De Boer, when treated as outlined, show an anomalous trend which appears to be too large to be caused by the vapor pressure of mercury at 100° C or by reasonable errors in the temperatures reported or in $T_0=273.16$. The value used for the coefficient of expansion of glass may be in error, or the cause may be a peculiar combination of errors in $p_{100°}$ and $p_{0°}$ at the lower densities, such as one measured after a compression and the other one measured after an expansion of the gas. Errors in the calibration of the piston gage are evidently not involved, since the ratio $p100°/p0°$ reduces to a ratio of weights applied.

observed values of pv/p_0v_0 quoted in table 7 apply to a constant mass of gas at a constant temperature, but in the least-squares solution to obtain eq 10.1 the mass of gas was obviously not restricted to constancy.

As an illustration of the effect on the coefficients and the deviations when this restriction is imposed and the same general form of equation is assumed, the equation

$$\frac{pv}{p_0v_0}=1+(53.033\pm0.58)\times10^{-5}\left(\frac{p}{p_0}-1\right)-4.802\times10^{-8}\left(\frac{p}{p_0}-1\right)^2 \qquad (10.2)$$

was obtained from the same data by least squares, giving equal weight to each observation. It may be noted from table 7 that the deviations from this equation are systematic, which suggests that another term is desirable. In fact, when the four different α's, eq 4.1 to 4.4, are computed from the measurements quoted in table 7 and plotted, a graph is obtained which is so similar to figure 2 in all respects, except for scale, that it is not reproduced here. For helium, as for hydrogen, α_2 appears to be linear in v_0/v over a wide range within the precision of the measurements. A least-squares equation for α_2 written as

$$\ln\frac{pv}{p_0v_0}=(53.212\pm0.44)\times10^{-5}\left(\frac{v_0}{v}-1\right)+8.000\times10^{-8}\left(\frac{v_0}{v}-1\right)^2 \qquad (10.3)$$

was obtained from the same measurements, weighting each observation proportional to $[(v_0/v)-1]$. It may be noted from table 7 that eq 10.3 is somewhat better than eq 10.1 or 10.2, according to the "Gauss" criterion sometimes used to express relative "closeness of fit" of different equations with a different number of coefficients. The random deviations from eq 10.3 suggest that no improvement may be expected from the use of additional terms. A graph, similar to figure 2, suggests that more terms must be used to represent α_1, α_3, or α_4 adequately.

TABLE 7.—*Data on helium at 0° C and 1 to 1,000 atmospheres obtained by Wiebe, Gaddy, and Heins*

$\frac{p}{p_0}$ (a)	$\frac{pv}{p_0v_0}$ (a)	$\frac{pv}{p_0v_0}$ calculated from equation—			Δ=(obs.−calc.) 10^5		
		eq 10.1	10.2	10.3	eq 10.1	eq 10.2	eq 10.3
1	1.0000	1.00101	1.00000	1.00000	+101	0	0
100	1.0523	1.05237	1.05203	1.05205	−7	+27	+25
200	1.1036	1.10338	1.10363	1.10359	+22	−3	+1
400	1.2026	1.20347	1.20395	1.20352	−87	−135	−92
600	1.3003	1.29967	1.30043	1.29948	+63	−13	+82
800	1.3924	1.39315	1.39308	1.39307	−75	−68	−67
1,000	1.4838	1.48353	1.48187	1.48336	+27	+193	+44
				$\left(\frac{\Sigma\Delta^2}{n-3}\right)^{\frac{1}{2}}$	±85	.....	.....
				$\left(\frac{\Sigma\Delta^2}{n-2}\right)^{\frac{1}{2}}$	.....	±123	±75

[a] Quoted from *J. Am. Chem. Soc.* **53**, 1721 (1931).

Measurements on helium at 0° C and up to 100 atmospheres obtained at the Reichsanstalt are quoted in table 8 and corrected, as previously explained in the section on oxygen. The data are insuffi-

cient to give an adequate value for the rate of change of α_3 with pressure, which has been assumed from eq 10.2 in obtaining the values of α at 1 atmosphere shown in the last column. The mean values of $10^5\ \alpha$, 52.5 and 53.0, are in good agreement with the corresponding values, 53.0 and 53.2, obtained in eq 10.2 and 10.3 from the measurements of Wiebe, Gaddy, and Heins.

Burnett [12] reported the results obtained in two concordant series of measurements with helium at 0° C, using two essentially identical metal containers, each with double walls, so that the pressures within and without the inner containers could be equalized. One container was evacuated and the other was filled with specially purified helium to a pressure of about 120 atmospheres. Opening an intercommunicating valve permitted equalization of pressure in the two inner containers. The valve was closed, one container was evacuated, and the process was repeated until the pressure was reduced to about 1 atmosphere after a series of six expansions. The unique feature claimed for the method is that the volumes of the two containers need not be measured and the two containers need not be exactly equal in volume. The calculations of the results, which appear to be straightforward, are too complex to reproduce here. Burnett gives an equation obtained by a "weighted least-squares method" which appears to amount to the following, in the symbols used here

$$\frac{pv}{p_0v_0}=1+52.430\times10^{-5}\frac{p}{p_0}. \tag{10.4}$$

This result, obtained with a radically different experimental procedure, appears to be in reasonably good agreement with the measurements of the Reichsanstalt and of Wiebe, Gaddy, and Heins.

TABLE 8.—*Data on helium at 0° C and 1 to 100 atmospheres obtained at the Physikalisch-Technische Reichsanstalt*

p	v	p_0	v_0	Observed $\frac{pv}{p_0v_0}$	Correction to $p_0=760$	Corrected $\frac{pv}{p_0v_0}$	$10^5\left(\frac{pv}{p_0v_0}-1\right)\Big/\left(\frac{p}{p_0}-1\right)$	$10^5\,\alpha^a$ at $p=p_0$
Holborn and Schultze[b], Ann. Physik **47**, 1089 (1915)								
*mm*Hg	*ml*	*mm*Hg	*ml*					
19, 229	110. 797	779. 54	2698. 51	1. 01279	1	1. 01280	52. 7	52. 8
19, 276	110. 796	781. 69	2697. 70	1. 01278	1	1. 01279	52. 5	52. 6
37, 794	110. 789	789. 02	5175. 17	1. 02543	2	1. 02545	52. 2	52. 4
38, 328	110. 790	800. 95	5168. 76	1. 02572	3	1. 02575	52. 1	52. 3
							Mean	52. 5
Holborn and Otto, Z. Physik **10**, 367 (1922)								
55, 873	106. 016	681. 74	8367. 9	1. 03833	−5	1. 03828	52. 8	53. 1
56, 304	106. 016	685. 91	8379. 2	1. 03858	−5	1. 03853	52. 7	53. 0
72, 991	106. 007	675. 66	10907. 8	1. 04988	−6	1. 04982	52. 4	52. 9
74, 497	106. 007	689. 95	10888. 7	1. 01523	−5	1. 05118	52. 7	53. 2
							Mean	53. 0

[a] Obtained from the data in the previous column and an estimated rate of change of α_3 with pressure, 4.8×10^{-3}, obtained from data of Wiebe, Gaddy, and Heins (see eq 10.2).

[b] The data on p and pv/p_0v_0 are quoted from Ann Physik **47**, 1089 (1915), the data on v, p_0 and v_0 are quoted from Z Physik **10**, 367 (1922) for the same values of p and pv/p_0v_0, which appears to establish that these details were omitted in the paper by Holborn and Schultze.

The more recent measurements on helium at 0° C and up to 12 atmospheres obtained at the Leiden Laboratory are quoted in table 9. In spite of the special efforts to avoid errors, described in Leiden Comm 227a and 227b, it is evident that the results are seriously affected by systematic errors, and are not in as good accord with more precise measurements made in other laboratories as might be expected from the description and calculations given. Keesom and Van Santen represented the measurements quoted in table 9 by a weighted least-squares equation, which in the symbols used here, is

$$\frac{pv}{p_0v_0}=1+50.28\times10^{-5}\left(\frac{v_0}{v}-1\right), \tag{10.5}$$

and the coefficient in this equation is stated to be accepted as "definitive" in connection with the present low-temperature scale used at the Leiden Laboratory. As mentioned previously, pressures were measured with a closed-end manometer, apparently filled with hydrogen. The so-called "normal volume," represented by v_0 here, is stated to be 548.861 cm^3 at 0° C, although actually measured "for practical reasons" at 18° C and corrected to 0° C. It is stated that a glass piezometer of 40-cm^3 capacity was immersed in an ice bath. A perusal of earlier communications, to which references are made, indicates that the 40-cm^3 piezometer when in the ice bath was probably connected by means of a flexible metal capillary to the top of a vertical glass tube (called the "stem of the piezometer" and stated to be 10.74 mm in diameter) maintained at 20° C in a stirred water bath. With mercury between the "stem" and the closed-end manometer, the helium in the piezometer and "stem" and the hydrogen in the closed end of the manometer were compressed to different pressures by means of auxiliary apparatus. At 6 atmospheres, more than half of the helium must have been at 20° C instead of 0° C. The exact manner of making the necessarily large correction does not appear to be given specifically in any of the communications examined, although similar measurements were made at 20° C, apparently for use in making such corrections. Uncertainties in the volume of the gas beneath a plane tangent to the mercury meniscus in the (10.74-mm diameter) "stem" were recognized, and mention is made of X-ray shadowgraphs taken of this meniscus.

TABLE 9.—*Data* [1] *on helium at 0° C and 1 to 12 atmospheres obtained by Keesom and Van Santen*

$\frac{p}{p_0}$	$\frac{v_0}{v}$	$\frac{pv}{p_0v_0}$	$\frac{10^3\left(\frac{pv}{p_0v_0}-1\right)}{\frac{v_0}{v}-1}$	Mean $10^3\alpha_1$
6.01487	6.00120	1.00228	45.6	46.0
6.02039	6.00632	1.00234	46.7	
6.05938	6.04541	1.00231	45.8	
6.75635	6.73732	1.00282	49.2	49.3
6.76536	6.74596	1.00288	50.1	
6.76787	6.74906	1.00279	48.5	
7.70765	7.67917	1.00359	53.8	52.7
7.71382	7.68803	1.00335	50.1	
7.69834	7.67063	1.00361	54.1	
9.94029	8.90267	1.00423	53.5	51.5
9.95584	8.92043	1.00397	50.1	
9.98098	8.94453	1.00405	51.0	
10.63712	10.58771	1.00467	48.7	50.3
10.64405	10.59301	1.00482	50.2	
10.65493	10.60214	1.00498	51.9	
11.48274	11.42075	1.00543	52.1	51.0
11.48867	11.42802	1.00531	50.9	
11.50026	11.44048	1.00523	50.1	
12.38806	12.32015	1.00551	48.7	49.1
12.43204	12.36263	1.00561	49.4	
12.45699	12.38790	1.00558	49.1	
12.46478	12.39543	1.00559	49.0	
			Mean	50.0 ±1.7

[1] Values in the first 3 columns are quoted from Leiden Comm. 227b (1933), regrouped according to values of p/p_0.

XI. NEON

Figure 4 illustrates an anomalous trend in α_2 obtained from measurements on neon reported by Michels and Gibson [13]. These measurements are among the earlier ones obtained in the Van der Waals laboratory by the method outlined in the section on hydrogen. The authors state their estimate of accuracy to be about 2 in 10^4, and the radii of the open circles have been chosen to indicate this uncertainty.

The Reichsanstalt measurements [14] on neon, designated by small black circles in figure 4, indicate the same normal trend in α_2 found for all the other gases considered. These measurements were corrected, as indicated previously in the section on oxygen. Glass containers were used in all of the Reichsanstalt measurements on gases previously discussed, with the same pressure inside and outside the glass, and small corrections were obviously applied for compression of the glass. In the measurements on neon, two different metal containers of the same diameter and wall thickness, but of different lengths, were used; and no corrections were made for the stretch of the containers with pressures up to 100 atmospheres inside and atmospheric pressure outside the containers. The metal containers were also used with nitrogen at temperatures up to 400° C, and measurements [15] were made at 0° C and also 100° C with the same pressure inside and outside the container, and also with atmospheric pressure outside. Apparently, the observed differences in volume were considered negligible for their purposes. The observed changes in volume are consistent with the value of 4.5×10^{-6} per atmosphere for

$(1/v)$ (dv/dp), calculated from the dimensions given and the elastic properties of the metal.

Attention is called to the lack of concordance in the values of v calculated from the relation $v=v_{0°}[1+at+bt^2]$ given for the volume of the metal container and the value of v actually used in the calculations [15] for the different gases at temperatures above 0° C. The metal container, constructed by welding ends on a cylindrical tube, was apparently not annealed before the initial calibration was made by filling with toluene at 18° C. After the container was used in measurements with several different gases at several different temperatures up to 400° C, a subsequent calibration [14] with mercury disclosed that the container had shrunk more than 2 in 10^3. A change in volume of this order of magnitude would make a considerable change in all the α's at 1 atmosphere or the "B-values" calculated from the measurements at various temperatures with He, A, N_2, H_2, and a mixture of Ne and He. It seems probable that most of the shrinkage took place during the measurements at the higher temperatures with one of these gases, but the order of the measurements with the different gases is not definitely stated. There is a strong implication that measurements with nitrogen were made first, although the anomalous results, mentioned but not recorded, with hydrogen at 300° C are in the right direction to be caused by such shrinkage; but this may also be explained satisfactorily on metallurgical grounds. The seriousness of this unfortunate situation is that these are the only available measurements on some of the gases at temperatures up to 400° C, and it shakes the very foundations for several equations of state and many other conclusions based upon these measurements.

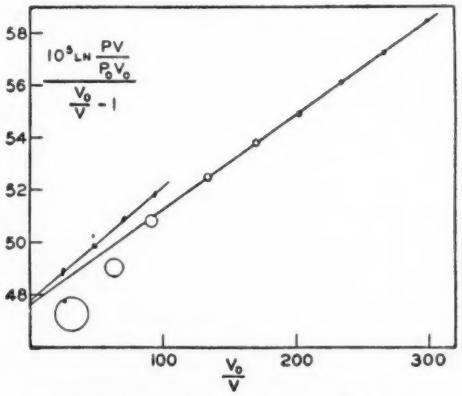

FIGURE 4.—*Data on neon at 0° C*

Reichsanstalt data, small closed circles; data of Michels and Gibson, open circles, with radii equivalent to uncertainty of 2 in 10^4 in pv/p_0v_0.

Uncertainties in the volume of the container at high temperatures in the measurements with neon [14] seem to be smaller than for the other gases, since rather convincing evidence is given that the container was adequately annealed by this time after numerous excursions to 400° C. Fortunately, the order is given in which the experiments on any one gas were made, and a good check with neon at 0° C is obtained before and after heating the container to 400° C. No corresponding check is supplied for the other gases. Using values of pv/p_0v_0 for nitrogen at 0° C up to 100 atmospheres, which were determined in glass containers and appear to be reliable to a few parts in 10^5, together with measurements on nitrogen at 0° C obtained with metal containers, leads to values for the volumes of the metal containers which are

about 2 in 10^4 larger than the values obtained in calibrations with mercury. This result appears to be in harmony with the results found by Kaminsky and Blaisdell [16], who demonstrated that mercury does not fill the small crevices in metal surfaces which are filled by gases. When allowance is made for slightly greater volumes of the metal containers and also for their stretch, the value of α at 0° C and 1 atmosphere obtained from the Reichsanstalt measurements on neon, indicated in figure 4, is about $49 \pm 1 \times 10^{-5}$.

A similar value with about the same uncertainty may be obtained from the measurements of Michels and Gibson by eliminating the reference state, $p_0 v_0$, at 0° C and 1 atmosphere and choosing one of the other states at higher pressures as a reference. When this is done, all the points indicated by the open circles in figure 4 are found to be represented by an equation of the form

$$\ln \frac{pv}{p_0 v_0} = A + \frac{Bv_0}{v} + C\left(\frac{v_0}{v}\right)^2, \tag{11.1}$$

well within the author's estimated limits of 2 in 10^4 and leads to the value for α at 1 atmosphere stated above. The fact that the points shown in figure 4 cannot be represented within these limits by the same form of equation, when the 1-atmosphere reference state is used as a basis for the calculations, appears to be very strong evidence of a systematic error in the earlier calibration of the piston gage or in the reference values, p_0, v_0, at 0° C and 1 atmosphere. It may be noted that, when the reference state is changed to a state at high pressures and the 1-atmosphere data are excluded, all the ratios used in the calculations with eq 11.1 are essentially ratios of weights applied to the piston gage, whereas in the calculations of α_2 shown in figure 4, the effective area of the piston gage is involved, as previously indicated in eq 5.8. The volume of the gas at 0° C and 1 atmosphere was apparently not measured directly but was calculated from a measurement at about 25° C and 1 atmosphere and corrected to 0° C in a manner described in several later papers from the same laboratory.

XII. REICHSANSTALT MEASUREMENTS BELOW 2 ATMOSPHERES

The latest measurements, obtained at the Reichsanstalt by Heuse and Otto [17] at 0° C and at pressures below 2 atmospheres, yield the following values for $10^5\alpha$:

p_0[1] (mm Hg)	He	H_2	N_2
533.10	59	72	−25
727.17	38	46	−62
994.50	58	63	−55
$10^5\alpha$ from previous sections for comparison	53.0	61.9	−45.3

[1] Throughout this section, p_0 is used to designate a reference state, sometimes called the ice-point pressure in a gas thermometer, in order to conform to common practice in gas thermometry. It should not be confused with the 1-atmosphere reference pressure used in other sections.

These measurements were made after many years of experience in such measurements, and after improvements in apparatus and technique had been developed. It is the purpose of this section to

investigate why these measurements yield such a wide scatter in α. There are reasons for expecting that the primary measurements of p and v at 0° C with the apparatus and method employed should have been capable of yielding a precision of the order of a few units in 10^6, which is comparable to about 1 percent in α, according to the analysis given in the section on uncertainties, when $[(p/p_0)-1]$ is about 0.3, as it is in all these measurements. The scatter, however, is many times this amount and appears to be systematic with the different gases at certain values of p_0.

The measurements were made at the same time and are reported in the same publication containing the latest determinations of pressure and volume coefficients of expansion of these gases in a gas thermometer over the fundamental interval, 0° to 100° C, which yield determinations of the thermodynamic temperature of the ice point, T_0. With each separate filling of the gas thermometer, measurements were made with a constant mass of gas in four different states, indicated in figure 5, where the point 0 is taken as the reference state for the group. Measurements at the states 1 and 0 yield a value for α or the slope of the 0° C isotherm. Similarly, measurements at the states 2 and 3 yield a value for the slope of the 100° C isotherm. Calculated values for the slope of the 100° C isotherm, for thermometer fillings to different p_0's, expressed in terms of $(10^5/v_0)(dpv/dp)$ are:

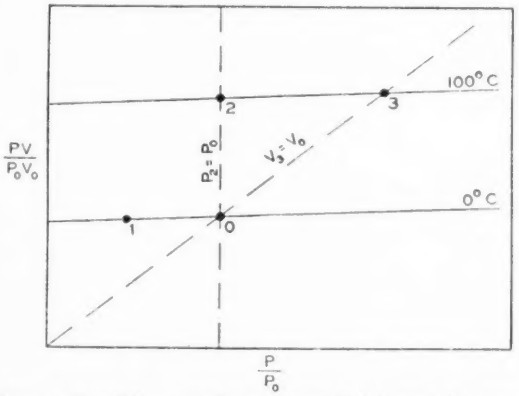

FIGURE 5.—*Diagram of a group of Reichsanstalt measurements with one filling of their gas thermometer.*

Measurements at states 0 and 2 were made at constant pressure and states 0 and 3 were measured at constant volume.

p_0 (mm Hg)	He	H_2	N_2
390.24	74	69	48
533.10	31	35	12
727.17	68	77	28
994.50	52	66	12
Mean	56	62	25

The scatter is greater than for the 0° C isotherm and departures from the mean appear to be systematic for all the gases at certain values of p_0.

In the Reichsanstalt calculations of T_0, the two isotherms were assumed to be straight lines, but the values used for the slopes were obtained from pv measurements up to 100 atmospheres. The assumption of straight lines and the measurements at the four states, indi-

cated in figure 5, are obviously sufficient to determine intersections of the two isotherms with the ordinate axis, which supply a value for

$$\frac{(pv)_{100}}{(pv)_0}=\frac{T_{100}}{T_0} \text{ and a value for } T_0=\frac{100}{\frac{T_{100}}{T_0}-1}.$$

When T_0 is calculated from the measurements in this very direct manner, the results turn out as shown in table 10 and also in figure 6, which again supplies unmistakable evidence of systematic departures from the mean value, represented by the horizontal line, for all the gases at certain values of p_0.

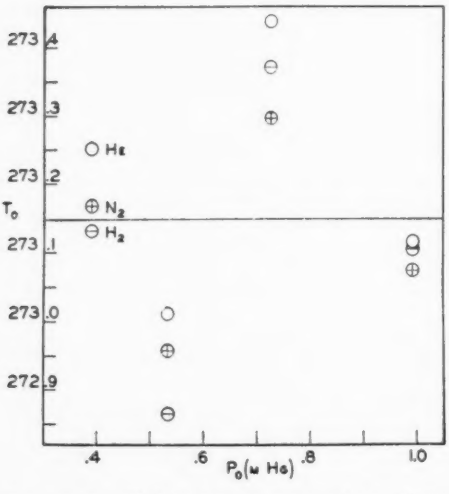

FIGURE 6.—*Values for the temperature of the ice point, T_0, on the thermodynamic scale calculated from the Reichsanstalt measurements on helium, hydrogen, and nitrogen quoted in table 10.*

The scatter of the values for T_0 is much greater than the scatter of the published values for T_0 obtained from calculations using values for the slopes determined from high-pressure measurements. Errors in the slopes determined by the low-pressure measurements are evidently magnified in the calculated values for T_0, since the same values for states 0, 2, and 3 in figure 6 are used in both methods of calculation. One method gets a value for T_0 from points 0 and 2, and another value from points 0 and 3, with "accepted" slopes, whereas the method used above requires all four points to get one value for T_0.

Arguments might be advanced that the direct method of calculation used in table 10 is the proper one to use, that the low-pressure measurements are sufficient in themselves, should stand on their own feet, and high-pressure pv data should be ignored, as is done under similar circumstances when measurements of p and ρ are made for purposes of atomic-weight determinations [1]. Magnification of errors, especially systematic errors in the slopes determined over a short interval, however, appears to make the other method of calculation, using slopes determined over a wide interval, the more reliable one to use. On the other hand, it may be argued that the measurements at state 1 are ignored and given no weight in the Reichsanstalt calculations of T_0, while equal weight is given to measurements at all four states in the calculations in table 10.

TABLE 10.—*Calculations to T_0 from Reichsanstalt measurements*

Date 1929	State (see fig. 5)	t	p [a]	v [a]	pv	$\frac{pv}{p_0v_0}$	$\frac{(pv)_{p=0}}{p_0v_0}$	$\frac{T_{100}}{T_0}$	T_0
					HELIUM				
		°C	*m Hg*	*cm³*	*m Hg-cm³*				
4/15	0	0	0.39024			1.000000	[b] 0.999727		
4/15	3	100	.53310			[a] 1.36611		1.365961	273.253
4/15	2	100	.39024			[a] 1.36597	1.365588		
4/13	1	0	.39024	425.624	166.0955	0.999889			
4/13	0	0	.53310	311.600	166.1140	1.000000	0.999586		
4/13	3	100	.72717			[a] 1.36602		1.366286	273.011
4/13	2	100	.53310			[a] 1.36594	1.365720		
4/12	1	0	.53310	428.199	228.2729	0.999903			
4/12	0	0	.72717	313.950	228.2950	1.000000	0.999636		
4/12	3	100	.99450			[a] 1.36611		1.365714	273.438
4/12	2	100	.72717			[a] 1.36587	1.365217		
4/10	1	0	.72717	426.301	309.9933	0.999797			
4/11	0	0	.99450	311.771	310.0563	1.000000	0.999245		
4/11	3	100	1.36280			[a] 1.36604		1.366146	273.115
4/11	2	100	0.99450			[a] 1.36579	1.365115		
					HYDROGEN				
6/4	0	0	0.39024			1.000000	[b] 0.999680		
6/4	3	100	.53310			[a] 1.36617		1.366122	273.133
6/4	2	100	.39024			[a] 1.36604	1.365685		
6/3	1	0	.39024	425.383	166.0015	0.999865			
6/3	0	0	.53310	311.431	166.0239	1.000000	0.999496		
6/3	3	100	.72717			[a] 1.36613		1.366482	272.865
6/3	2	100	.53310			[a] 1.36604	1.365793		
6/1	1	0	.53310	426.572	227.4055	0.999881			
6/1	0	0	.72717	312.764	227.4326	1.000000	0.999554		
6/1	3	100	.99450			[a] 1.36620		1.365805	273.370
6/1	2	100	.72717			[a] 1.36593	1.365196		
5/30	1	0	.72717	426.938	310.4565	0.999777			
5/30	0	0	.99450	312.243	310.5257	1.000000	0.999171		
5/31	3	100	1.36280			[a] 1.36621		1.366159	273.105
5/31	2	100	0.99450			[a] 1.36589	1.365026		
					NITROGEN				
4/4	0	0	0.39024			1.000000	[b] 1.000234		
4/4	3	100	.53310			[a] 1.36673		1.366074	273.169
4/4	2	100	.39024			[a] 1.36664	1.366394		
4/9	1	0	.39024	427.567	166.8537	1.000047			
4/9	0	0	.53310	312.973	166.8459	1.000000	1.000175		
4/9	3	100	.72717			[a] 1.36671		1.366356	272.959
4/9	2	100	.53310			[a] 1.36668	1.366595		
4/6	1	0	.53310	427.205	227.7430	1.000159			
4/5	0	0	.72717	313.141	227.7067	1.000000	1.000596		
4/5	3	100	.99450			[a] 1.36709		1.365904	273.296
4/5	2	100	.72717			[a] 1.36699	1.366718		
4/6	1	0	.72717	428.357	311.4884	1.000192			
4/8	0	0	.99450	313.151	311.4287	1.000000	1.000714		
4/8	3	100	1.36280			[a] 1.36740		1.366203	273.073
4/8	2	100	0.99450			[a] 1.36734	1.367178		

[a] Quoted values, all others are calculated values.
[b] Since measurements at state 1 were lacking, a value for the slope of the 0° isotherm was assumed in order to get at value for T_0 from this group.

A third method of calculation appears to have several advantages in this particular case, since it retains certain desirable features of each of the other methods and removes many of the systematic effects already mentioned by ignoring certain calibration measurements which are not described in detail, and uses instead measurements at state 1, thereby giving them considerable weight. In this method, the apparently more reliable values for the slopes supplied by high-pressure data are employed, as is done in the Reichsanstalt method, but are inserted into the calculations at an earlier stage in combination with measurements at states 1 and 0, figure 5. If such measurements yield an erroneous value for the slope at 0° C, and if the errors are random or accidental, the chances are even that the measurements at state 0 may be in error and hence may lead to two erroneous values[10] for T_0 in the Reichsanstalt method of calculation, which in effect gives this point double weight, because it is used in calculating a constant-volume and also a constant-pressure coefficient of expansion, and with accepted slopes, two separate values for T_0. On the other hand, if the measurements at states 1 and 0 appear to be systematically in error, it is obviously desirable to make the calculations so as to eliminate the effect of the systematic errors.

The unique feature of the latest Reichsanstalt measurements, which is supposed to make them more reliable than similar earlier measurements leading to $T_0=273.20$, was the use of a specially constructed mercury manometer, which was surrounded by ice. Several platinum wires were sealed into the glass walls at certain chosen heights and bent downward at the axis of a long vertical glass tube to serve as "prick points" at the center. Thus all of the pressure measurements were made with definite fixed heights of mercury columns, as indicated in table 10. The exact manner in which these heights were measured, once and for all, is not clearly described. It is mentioned, however, that the distances between prick points were measured at room temperature, although as used the manometer was at 0° C. It is mentioned further that only pressure ratios are important and that the above circumstance should introduce no appreciable error in the ratios of heights, which would appear to be true if there were no vertical temperature gradients during the measurements at room temperatures, if the sealing-in processes at several points had no effect, and if the coefficient of linear expansion of the glass was the same throughout. No information is supplied relative to possible refraction errors in sighting through possibly nonuniform glass walls to the prick points or onto the mercury surface brought into "optical contact" with the prick points in the calibration of the manometer. All of these and other uncertainties in the calibration of the manometer, which appear to be the source of the systematic effects previously mentioned, may be eliminated as outlined below.

Although Heuse and Otto apparently did not realize it, they had at their disposal in reality, almost every day they took observations extending over a period of several months, an independent and reasonably reliable partial calibration of their manometer with each filling of their gas thermometer. Instead of inserting accepted values for slopes into the calculations near the end as they did, everything

[10] A possible illustration of this is in the case of N_2 at $p_0=390$ mm (see Heuse and Otto's table 7), where the reported values give for T_{100}/T_0, 1.36616 (constant pressure) and 1.36619 (constant volume), while the mean value for the 3 gases is 1.36609.

would have come out better if they had inserted the accepted slopes at 0° C into the manometer calibration at the beginning. Instead of using the measured heights in the calibration of the manometer to calculate 0° C slopes, which scatter widely and were not used in the calculations later on, the same calculations may be reversed, since measurements at states 1 and 0, together with accepted slopes for the different gases, lead directly to several calibrations of the manometer. Although such calibrations yield only pressure ratios, these are the important quantities anyway.

Equation 4.3, together with the assumption of constant slope over the small interval covered by these measurements, gives

$$\alpha=\frac{1}{v_0}\left(\frac{dpv}{dp}\right)_t=\frac{1}{v_0}\left(\frac{p_bv_b-p_av_a}{p_b-p_a}\right)_t, \tag{12.1}$$

where the subscripts refer to any two equilibrium states, a and b, of a given mass of gas at 0° C, and v_0 is the volume of the same mass of gas at 0° C and 1 atmosphere, which takes the place of a mass determination. All the values of α at 1 atmosphere, obtained in previous sections, are on this same basis and hence may be used to advantage in eq 12.1 or any transformation of it. This is emphasized because the later calculations are made to serve a double purpose, one of which is to obtain a test of the reliability of the values of α for the different gases.

In order to get eq 12.1 into a convenient form for the calculations at hand, the following steps are written out

$$p_bv_b-p_av_a=\alpha v_0(p_b-p_a)$$

$$p_b(v_b-\alpha v_0)=p_a(v_a-\alpha v_0)$$

$$\frac{p_b}{p_a}=\frac{v_a-\alpha v_0}{v_b-\alpha v_0}$$

$$\frac{p_b}{p_a}=1+\frac{v_a-v_b}{v_b-\alpha v_0}, \tag{12.2}$$

In the Reichsanstalt measurements, the quantity (v_a-v_b) was directly measured by weighing displaced mercury, which is one of the simplest and most accurate of laboratory measurements. The quantity v_b was obtained from similar measurements of the volume of the gas-thermometer bulb and the connecting glass tubing up to the lower mercury surface in the manometer. Using the measured volumes quoted in table 10, and values for v_0 to four figures, easily obtainable from the column headed pv, and the values of α previously obtained, the following results are given in detail as an illustration.

Date	Gas	$10^3\alpha$	αv_0	v_b	$v_b-\alpha v_0$	v_a-v_b	$\frac{p_b}{p_a}$
4/12	He	53.0	0.1592	313.950	313.7908	114.249	1.364093
6/1	H_2	61.9	.1852	312.764	312.5788	113.808	1.364094
4/5	N_2	−45.3	−.1357	313.141	313.2767	114.064	1.364100
Mean							1.364096

These results supply the best direct experimental evidence available that the values for the slopes of the 0° C isotherms below 2 atmospheres for these three gases are mutually consistent within reasonable uncertainties in these measurements. The maximum deviation from the mean ratio p_b/p_a is about 3 in 10^6, which appears to confirm the earlier statement that a precision of this order of magnitude should have been attainable in these measurements. To attain such a precision, of course, means that the two mercury surfaces in the manometer must be set in "optical contact" with the prick points with a precision of about 0.002 mm,[11] in the foregoing instances, since the recorded pressures quoted in table 10 are 533.10 and 727.17 mm Hg. But the ratio of these numbers obtained from measurements of heights in the initial calibration of the manometer is $p_b/p_a=1.364041$. This value is different from the above mean by 40 in 10^6, which corresponds to a systematic error of about 30 percent in all the α's, 0.017 cm^3 in v_a-v_b, (0.23 g Hg) or 0.047 cm^3 in v_b (0.64 g Hg), all of which appear to be unreasonably large. It seems more likely that the height measurements in the initial calibration are responsible for the difference.

When the same calculations are carried out, using all the reported volume measurements, including oxygen ($10^5\ \alpha=-95.1$) and neon ($10^5\ \alpha=49.0$), the results indicate a lower precision in several instances, as shown below.

Calibration based on measurements of heights

p_b	533. 10	727. 17	994. 50	1362. 80
p_a	390. 24	533. 10	727. 17	994. 50
p_b/p_a	1. 366082	1. 364041	1. 367631	1. 370035

Calibrations based on isothermal slopes and measurements of volume, reported in Heuse and Otto's table 2

He	1. 366067	1. 364093	1. 367608	--------
H_2	1. 366056	1. 364094	1. 367624	--------
N_2	1. 366031	1. 364100	1. 367675	--------
O_2	1. 366076	1. 364081	1. 367651	--------
Ne	--------	--------	1. 367650 [12]	--------
Mean	1. 366057	1. 364092	1. 367642	--------

Calibration based on isothermal slope and measurements of volume, dated 2/6/1929 and reported in Heuse and Otto's table 1

He	1. 366000	1. 363969	1. 367720	1. 370275

There appears to be no convincing evidence in these results that the value used for α for any one gas is inconsistent with the values for the other gases. The scatter for the different gases at the third pressure ratio is about twice as large as at the other two ratios. One possible reason for this may be that a much longer piece of capillary tubing containing mercury at room temperature was used in the measurements of v_a-v_b when the pressure exceeded 1 atmosphere. Furthermore, it may be noted from table 10 that the two states for He giving the lowest value (1.367608) were measured 1 day apart, and the two states for N_2 giving the highest value (1.367675) were measured 2 days apart, whereas the two states were measured on the same day for all the other gases at the corresponding ratio.

[11] The author has had some experience which indicates that prick point settings on a mercury surface can be made to this precision without much difficulty.

[12] Calculated from volume measurements reported in Ann. Physik **6**, [4] 778 (1930).

In the calibration calculated from the measurements, dated February 6, 1929, the conditions were different. These measurements were obtained before the gas-thermometer bulb (v=297.134 cm^3) was sealed onto the capillary tubing. All these measurements were made with one He filling (v_0=70.38 cm^3) and the mercury displacements were smaller (14.528 to 36.709 cm^3). Heuse and Otto do not give the diameter of the manometer tubing, but state that a change of 0.1 mm in the height of the mercury meniscus corresponds to a change of 0.005 cm^3 in the volume of the gas beneath a fixed plane tangent to the mercury meniscus. All the differences from the means given above correspond to differences in the meniscus height in the two states of less than 0.2 mm, including the February 6, 1929, calibration. It seems likely that much of the scatter may be appropriately charged to differences in meniscus height rather than to corresponding errors up to 0.010 cm^3 (0.14 g Hg) in the volume measurements.

When the mean values for the pressure ratios determined with several gases are used in later calculations, most of the systematic effects previously mentioned are removed, the scatter is markedly reduced, and there is general improvement all along the line. For example, the constant-volume coefficients for N_2 are brought into much better agreement with the measurements reported by Beattie [11]. While the constant-volume coefficients, β_v, are changed, the constant-pressure coefficients, β_p, are unchanged. The improvement in the differences, $\beta_p-\beta_v$, which are related to the 100° C isotherm slopes, is illustrated below.

As reported (height calibration)				Gas volume calibration	
p_0	$10^7\beta_p$	$10^7\beta_v$	$10^7(\beta_p-\beta_v)$	$10^7\beta_v$	$10^7(\beta_p-\beta_v)$
HELIUM					
mm Hg					
390	36, 597	36, 611	14	36, 608	11
533	36, 594	36, 602	8	36, 607	13
727	36, 587	36, 611	24	36, 612	25
994	36, 579	36, 604	25	36, 604	25
HYDROGEN					
390	36, 604	36, 617	13	36, 614	10
533	36, 604	36, 613	9	36, 618	14
727	36, 593	36, 620	27	36, 621	28
994	36, 589	36, 621	32	36, 621	32
NITROGEN					
390	36, 664	36, 673	9	36, 670	6
533	36, 668	36, 671	3	36, 676	8
727	36, 699	36, 709	10	36, 710	11
994	36, 734	36, 740	6	36, 740	6

Calculations of a mean value for T_0 and an uncertainty in T_0 from these Reichsanstalt measurements on the basis of a different manometer calibration have not been carried out for several reasons. It requires a recalculation of all of the foregoing values to one more place. Uncertainties in the values of the difference between the 0 and 100 °C isotherm slopes are involved, as are questions of weighting. It

appears, however, that the major change is a smoothing of the data and a reduction in the calculated uncertainty without much change in the mean value for T_0. On the basis of these 1929 measurements, Heuse and Otto reported a mean value of $10^8\beta=366{,}086$, which corresponds to $T_0=273.160$. Combining these with previous measurements, they reported a weighted mean of $10^8\beta=366{,}076$, which corresponds to $T_0=273.167$.

XIII. MEASUREMENTS BY BAXTER AND STARKWEATHER

It is the purpose of this section: (1) to demonstrate that the measurements of Baxter and Starkweather obtained at 0° C and 1 atmosphere or less are in substantial agreement, or at least do not seriously conflict, with the values of α already obtained from high-pressure measurements within the calculated uncertainties of the two sets of measurements; and (2) to illustrate that the calculated uncertainties in values for atomic weights and RT_0, based entirely on measurements at 0° C and 1 atmosphere or less, are larger than the calculated uncertainties based on both sets of measurements.

In the previous sections, the calculated uncertainties in α at 1 atmosphere were about 1 percent or less. It was pointed out in section V that 1 percent in α was comparable to about 5 in 10^6 in pv/p_0v_0 for these gases over a range of ½ atmosphere. As shown in table 11, the measurements of Baxter and Starkweather, which appear to be among the most precise measurements of this kind available, the calculated uncertainties in pv/p_0v_0 exceed the amount stated above and the calculated uncertainties in the α's range from 7 to 30 percent. In every case, however, the values of α obtained from high-pressure measurements are well within the calculated limits of uncertainty in the low-pressure measurements, as shown below.

$10^4\,\alpha$ from measurements at—			Differences in mean values (%)
Gas	High pressures	Low pressures	
O_2	−95.1±0.9	−93±7	−2
N_2	−45.3±0.3	−41±9	−12
Ne	49 ±1	59±16	−20
A	−94 ±1	−89±12	−5

The measurements of Baxter and Starkweather were apparently made by weighing all of these gases in glass "globes" of about 2-liter capacity, using the same manometer and technique throughout all these measurements. The constant sign of the differences between the mean values of α suggests the possibility of a systematic error in the measurements of density or pressure or both. According to the analysis given in section V, 2 percent in α for O_2 corresponds to about 0.004 mm Hg in p, or about 0.02 mg in the weighings of 2-liter globes. That the difference is this small is high tribute to the care and skill of the observers.

TABLE 11.—*Measurements of the density of gases at 0°C obtained by Baxter and Starkweather*

$\frac{p}{p_0}$	Pressure	Density	Uncertainty $\frac{10^6 u}{\rho}$	No. obs.	$\frac{pv}{p_0 v_0}$	$\frac{10^3\left(\frac{pv}{p_0 v_0}\right)-1}{\frac{p}{p_0}-1}$ $10^3\alpha_1$	Uncertainty
	OXYGEN (PROC. NTL. ACAD. SCI. **12**, 703 (1926))						
	mm Hg[a]	g/liter					%
1	760	1.428962±10[b]	7	6	1.000000±00	.....	90
3/4	570	1.071485±29	27	20	1.000220±28	−88.0	13
1/2	380	0.714154±24	34	12	1.000458±35	−91.6	8
1/4	190	.356985±17	48	10	1.000716±48	−95.5	7
					Weighted [c] mean..	−93±7	
	NITROGEN (PROC. NTL. ACAD. SCI. **12**, 703 (1926))						
1	760	1.250361±29	23	18	1.000000±00	.....	...
2/3	506.667	0.833482±16	19	18	1.000110±30	−33.0	27
1/3	253.333	.416662±16	38	14	1.000290±44	−43.5	15
					Weighted [c] mean..	−41±9	
	NEON (PROC. NTL. ACAD. SCI. **14**, 57 (1928))						
1	760	0.899902±20	22	17	1.000000±00	.....	...
2/3	506.667	.600044±30	50	11	0.999818±55	54.6	30
1/3	253.333	.300090±26	87	12	0.999591±90	61.5	22
					Weighted [c] mean..	59±16	
	ARGON (PROC. NTL. ACAD. SCI. **14**, 57 (1928))						
1	760	1.783640±44	25	15	1.000000±00	.....	...
2/3	506.667	1.188739±45	38	7	1.000299±45	−89.7	15
1/3	253.333	0.594193±30	51	6	1.000594±72	−89.1	12
					Weighted [c] mean..	−89±12	

[a] At 0° C and g=980.616.

[b] In stating these uncertainties the decimal point has been disregarded for convenience. Thus 1.428962±10 is to be interpreted as 1.428962±0.000010.

[c] Weighting each α_1 inversely as the square of its uncertainty.

In figure 7, uncertainties in the measurements are indicated by arrows. If arrows indicating uncertainties in the values of α for O_2 and A had been shown in figure 1, the apparent inconsistency between low- and high-pressure measurements would be more readily understandable. It is evident from table 11, and also figure 7, that the uncertainties increase at the lower pressures and become magnified at p=0, where the highest accuracy is most desirable. The unbroken lines in figure 7 represent least-squares equations based entirely on the measurements of Baxter and Starkweather, "weighted according to their probable errors," as stated in the 34th annual report [18] of the committee on atomic weights. The broken lines represent the 0° C isothermal slopes or α's obtained in previous sections.[13]

[13] The data on argon fall so close to the oxygen line in figure 7 that they were omitted to avoid confusion.

Mean values for ρ_0 and values for RT_0 and M may be calculated from the measurements quoted in table 11, as has been done by Baxter and Starkweather [18]. Similarly, values for ρ_0, RT_0 and M may be

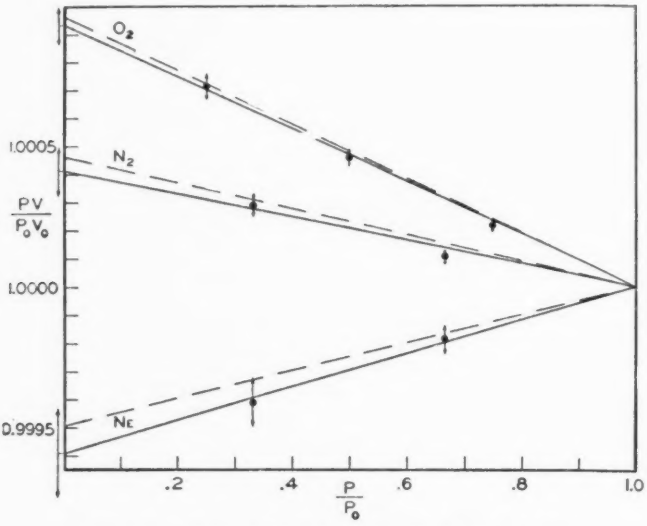

FIGURE 7.—*Data at 0° C by Baxter and Starkweather.*

Arrows indicate calculated uncertainties. Unbroken lines based on low-pressure measurements. Broken lines represent slopes calculated from high-pressure measurements.

calculated by using the values of α previously obtained. The differences in the calculated uncertainties in the two cases may be of interest.

Equations 3.3 and 4.3 combined with $p=0$, yield

$$pv=p_0v_0(1-\alpha)=\frac{RT_0}{M}, \tag{13.1}$$

which may be written, for these calculations, in the equivalent forms

$$RT_0=\frac{Mp_0(1-\alpha)}{\rho_0} \tag{13.2}$$

$$M=\frac{\rho_0 RT_0}{p_0(1-\alpha)}. \tag{13.3}$$

Based entirely on the measurements of Baxter and Starkweather, the results turn out as follows:

$$RT_0=\frac{32(1.00093\pm 7)}{1.428965\pm 10}=22.4147\pm 16$$

$$M(\mathrm{N_2})=\frac{(1.25037\pm 2)(22.4147\pm 16)}{1.00041\pm 9}=28.0152\pm 32$$

$$M(\mathrm{Ne})=\frac{(0.89990\pm 2)(22.4147\pm 16)}{0.99941\pm 16}=20.1829\pm 36$$

$$M(\mathrm{A})=\frac{(1.78364\pm 4)(22.4147\pm 16)}{1.00089\pm 12}=39.9442\pm 56$$

When the α's obtained from high-pressure measurements are used, the calculated uncertainties are reduced, as follows:

$$RT_0=\frac{32(1.000951\pm 9)}{1.428965\pm 10}=22.4151\pm 3$$

$$M(N_2)=\frac{(1.25039\pm 2)(22.4151\pm 3)}{1.000453\pm 3}=28.0149\pm 6$$

$$M(Ne)=\frac{(0.89990\pm 2)(22.4151\pm 3)}{0.99951\pm 1}=20.1812\pm 6$$

$$M(A)=\frac{(1.78364\pm 4)(22.4151\pm 3)}{1.00094\pm 1}=39.9430\pm 11$$

For comparison, the 1940 international atomic weights give 28.016 for N_2, 20.183 for Ne and 39.944 for A, the last two values apparently being based entirely on the measurements quoted in table 11. When consideration is given to the results of other observers and different values are used for ρ_0 and the estimated uncertainty in ρ_0, the results are slightly different,[14] of course, but the major uncertainty in all published atomic weight calculations of this kind is in the value of α determined by low-pressure measurements alone.

It should be noted from table 11 that the pressure unit is 760 mm Hg at 0° C and g=980.616. Expressing the above results for RT_0 in different units gives

22.4151 liter mole^{-1} atm (g=980.616)
22.4140 liter mole^{-1} atm (g=980.665)
22414.6 cm^3 mole^{-1} atm (g=980.665)
2271.16 joules mole^{-1}

XIV. CONCLUSION

As a result of many careful and painstaking investigations in recent years, the slopes of the *pv* isotherms at 0° C below 2 atmospheres for He, Ne, A, H_2, N_2, and O_2 appear to be known to about 1 percent, which is comparable to a few parts in a million in relative measurements of pressure and volume at this temperature and in this pressure range. Reliable values for the isothermal slopes are of importance in atomic-weight determinations, in gas thermometry, in certain theoretical calculations, in gas analyses (for example, in converting from volume percent to mole percent), and in many other applications where it is desired to avoid the approximations involved in the ideal gas laws.

Some of the summaries relative to these slopes, such as those given in International Critical Tables, in the Handbuch der Experimental Physik, and in the most recent summary by Keesom and Tuyn [10] give the impression that these slopes are very uncertain because of the wide scatter in the published values obtained by different observers. It is hoped that the foregoing discussion of the subject may supply the key to some of the reasons for such a wide spread in the published values.

[14] Birge [2] used the same value of ρ_0 for O_2. He used "least-squares probable error" apparently in his ± terms. Putting these on the basis used here (see section V), his "adopted values" for ρ_0 and α lead to

$$RT_0=\frac{32\ (1.000927\pm 90)}{1.428965\pm 90}=22.4146\pm 24 \text{ liter mole}^{-1}\text{ atm } (g=980.616.)$$

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COMPARATIVE TESTS OF CHEMICAL GLASSWARE

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ABSTRACT

This paper describes the results of comparative tests of four brands of chemical glassware: Tamworth-Glasbake, Kimble No. N51a, chemical Pyrex, and Vycor (Corning Glass Works' 96-percent silica glass No. 790). The wares were compared with respect to resistance to acid, alkaline, and nearly neutral reagents, and resistance to thermal and mechanical shock. The chemical composition and the thermal expansivity of each glass were also determined.

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I. INTRODUCTION

Three brands of borosilicate glass, varying somewhat in composition and general properties, are now produced in the United States in the form of beakers, flasks, and other apparatus for general laboratory use. These three wares are chemical Pyrex (Corning Glass Works' No. 774); Kimble Glass Co.'s No. N51a; and Tamworth-Glasbake.[1]

A series of tests designed to determine the relative resistance to chemical attack of these three wares has been made at the National Bureau of Standards, similar to tests made about 25 years ago,[2] when the European wares commonly used up to that time began to be displaced by several products of American manufacturers. The chemical compositions of the glasses, and their thermal coefficients of expansion, were also determined, and some information gained concerning their resistance to mechanical and thermal shock.

[1] The ware bearing this mark is manufactured by the McKee Glass Co., Jeannette, Pa., and distributed by Tamworth Associates, Needham Heights, Mass. The McKee Glass Co. has stated that ware of the same composition will be distributed in certain parts of the country under the mark "Glasbake."

[2] Percy H. Walker and F. W. Smither, *Comparative tests of chemical glassware*, Tech. Pap. BS **10**, (1918) T107; J. Ind. Eng. Chem. **9**, 1090 (1917).

A new type of chemical glassware sold under the trademark Vycor (Corning Glass Works' 96-percent silica glass No. 790) was included in some of the tests.

Erlenmeyer flasks of 250-ml capacity were used for nearly all the tests described in this report. The factories where the different glasses are produced were visited by one of the authors to see the flasks made (except the Vycor) and to earmark them for delivery to the Bureau. At the same time, samples of the glasses in the form of rods were prepared and brought to the Bureau. These samples, together with some in the form of slabs, were used for some of the measurements of the thermal expansivity.

II. CHEMICAL COMPOSITION

The major constituents of the glasses tested were determined by routine chemical analyses.[3] The results obtained, as given in table 1, are intended to show the approximate composition, except with respect to arsenic and antimony. These elements were determined with greater care.[4]

TABLE 1.—*Composition of the samples*

Constituent	Glasbake	Kimble	Pyrex	Vycor[d]
	Percent	*Percent*	*Percent*	*Percent*
SiO_2	78. 4	74. 7	81. 0	96. 3
B_2O_3	14. 0	9. 6	13. 0	2. 9
R_2O_3[a]	2. 5	5. 6	2. 2	0. 4
ZnO	n. d.[c]	0. 1	n. d.	n. d.
CaO	0. 1	. 9	neg.[b]	neg.
BaO	n. d.	2. 2	n. d.	n. d.
MgO	neg.	neg.	n. d.	n. d.
Na_2O	5. 0	6. 4	3. 6	<0. 02
K_2O	neg.	0. 5	0. 2	< . 02
As_2O_3	0. 037	. 027	. 002	. 005
Sb_2O_3	. 038	. 009	n. d.	n. d.

[a] Chiefly Al_2O_3.
[b] "neg." indicates a negligible amount of the constituent.
[c] "n. d." indicates the corresponding constituent was not detected.
[d] 0.3 percent of undetermined constituents.

III. THERMAL EXPANSIVITY

The average coefficient of linear expansion in the range 20° to 300° C was determined with the apparatus described by Souder and Hidnert[5] on specimens of the rods obtained for that purpose. The coefficient was also determined by the interferometer method described by Peters and Cragoe,[6] as amplified by Saunders,[7] on specimens cut from slabs and from flasks. The rods were tested first "as received" (i. e., air-cooled or unannealed), and again after the same specimens

[3] Analyses made by Francis W. Glaze.
[4] Determinations made by J. A. Scherrer.
[5] Wilmer Souder and Peter Hidnert, *Measurement on the thermal expansion of fused silica*, BS Sci. Pap. 21, 1 (1926) S524. The measurements by this method were made by Hidnert.
[6] C. G. Peters and C. H. Cragoe, *Measurements on the thermal dilatation of glasse sat high temperatures*, BS Sci. Pap. 16, 449 (1920) S393.
[7] James B. Saunders, *Improved interferometric procedure with application to expansion measurements*, J. Research NBS 23, 179 (1939) RP1227. The measurements by this method were made by L. H. Maxwell and by Saunders.

were carefully annealed. The annealing consisted in heating the rods to 590° C for 5 hours, cooling to 515° C at the rate of 8° C per hour, holding at the latter temperature for 48 hours, and then cooling slowly to room temperature. The initial cooling rate from 515° C was about 1° C per hour and was gradually increased to a maximum of 10° C per hour as the temperature fell.[8]

The results of the expansivity measurements are given in table 2. The data show that the two methods of measurement give practically identical results, unless there were compensating differences in the samples and methods used.

TABLE 2.—*Average coefficient of linear expansion* $\times 10^6$, *between 20° and 300° C*

Condition	Brand of glassware			
	Glasbake	Kimble	Pyrex	Vycor
As received	[a]3. 7(H)	4. 9(H)	3. 3(H)	0. 8(S)
Do	3. 7(M)	4. 9(M)	3. 3(M)	----
Annealed	3. 4(H)	4. 8(H)	3. 0(H)	----
Do	3. 6(M)	4. 9(M)	3. 1(M)	----

[a] Values followed by (H) were obtained by P. Hidnert, those followed by (M) by L. H. Maxwell, and that followed by (S) by J. B. Saunders.

IV. RELATIVE CHEMICAL RESISTANCE

In studying the effect of various aqueous solutions and other reagents on the glasses, no attempt was made to determine the nature of the reactions, that is, to find out what changes occurred at the surface of the glass or whether the material removed was of the same composition as the glass. An exception to this general rule was made in determining the amount of arsenic removed by alkaline solutions, since this is of known interest in certain uses of chemical glassware, such as in the determination of arsenic in insecticide residues on fruits. These results appear in table 5, footnote a.

In general, it appeared that the analyst's interest would lie in the total amount of substance removed from the glass, in relation both to the contamination of solutions undergoing analysis, and to the relative rates at which the wares would become unserviceable through roughening of the surface. Because precipitates tend to adhere to etched glass surfaces so tenaciously as to make quantitative transfers difficult or impossible, the useful life of much chemical glassware may be ended by excessive etching or scratching of the inner surfaces, rather than by breakage.

Since the chemist cannot readily have glassware made to order (with respect to composition or properties) but must necessarily make a choice among products that are commercially available, it seemed useless to attempt to devise tests that might yield results which would be independently reproducible and which might have some absolute significance. Instead, the methods of testing chemical resistance were

[8] It happened to be convenient to anneal the rods in the same furnace with some optical glass—hence this unnecessarily long schedule.

planned solely to yield comparative results. The three brands (all except the Vycor) were always treated simultaneously, thus making it unnecessary to define the conditions of treatment very closely. All of the tests of chemical resistance were made on samples taken from a single lot of 250-ml Erlenmeyer flasks of each type of ware. It is possible that similar tests made on other lots of the wares and in other laboratories would not yield the same numerical results as those reported here, but it is believed that, barring significant changes of composition in any of the wares, similar tests would give the same relative results.

All the flasks used were numbered for identification. They were prepared for testing by gentle scouring, inside and out, with a pumice soap, thorough rinsing with distilled water, heating overnight in an electrically heated oven at about 110° C, and weighing. Prior to weighing they were placed near the balance in a covered box for several hours and then placed, three at a time (together with a tare flask) within the balance case for at least half an hour. One flask of each type, similarly treated, was used as the tare. The tare flasks were rinsed and dried before each set of weighings and were scoured only between tests with different reagents.

By taking pains in handling the flasks and in protecting the air of the balance case from sudden changes in temperature or humidity, the observed weights were reproducible, with rare exceptions, within 0.1 or 0.2 mg. Losses in weight caused by scouring and rinsing the flasks were negligible. These conclusions were reached from a series of repeated weighings of flasks not treated, except by cleaning and drying, which are shown in table 3. In this series the tare flasks were not scoured, but only rinsed and dried whenever the others were scoured, rinsed, and dried.

TABLE 3.—*Repeated weighings [a] of flasks to determine precision of weighing*

Treatment	Relative humidity	Glasbake [b]		Kimble [c]			Pyrex [d]		
		No. 13	No. 14	No. 15	No. 22	No. 23	No. 24	No. 15	No. 16	No. 17
	%	g	g	g	g	g	g	g	g	g
Scoured, etc	11	16. 5285	13. 6856	2. 7927	2. 2975	2. 4775	5. 8355	0. 6991	7. 1825	5. 0996
Do	6 to 14	16. 5285	13. 6858	2. 7927	2. 2976	2. 4777	5. 8355	. 6990	7. 1825	5. 0995
Reweighed after standing 3 hr	14	16. 5285	13. 6857	2. 7928	2. 2975	2. 4775	5. 8355	. 6990	7. 1825	5. 0995
Reweighed after standing overnight	16 to17	16. 5285	13. 6858	2. 7926	2. 2975	2. 4775	5. 8355	. 6990	7. 1825	5. 0995
Scoured, etc	34 to 38	16. 5285	13. 6860	2. 7928	2. 2976	2. 4776	5. 8355	. 6990	7. 1822	5. 0996

[a] The weights are the difference between each flask and the corresponding tare flask.
[b] The weight of the tare flask was 78 g.
[c] The weight of the tare flask was 58 g.
[d] The weight of the tare flask was 76 g.

With a few exceptions, which will be indicated, 200 ml of the selected reagent was placed in each of three flasks of each of the wares, which were heated simultaneously on an electric hot plate. Gentle boiling was maintained for 6 hours. During the treatment, each flask was closed with a funnel-shaped cover, made of the same glass, to serve as a partial condenser. Flattened pellets of gold sponge served admirably to prevent bumping and were not attacked by any of the reagents except perchloric acid, which did attack them slightly. About midway of the 6-hour period of boiling, the volume of reagent was restored to about 200 ml by replenishing with hot water, except as otherwise noted. The flasks made of the different glasses were so nearly of the same shape and capacity that variations in the surface exposed to attack were regarded as negligible. Because they were exposed to condensing vapors and to spray from the boiling liquid, the glass surfaces above the level of the reagent were also attacked, although probably not equally with the submerged portions.

After the 6-hour treatment, the flasks were emptied, rinsed with water, gently scrubbed inside and out, then thoroughly rinsed again, and heated in the oven overnight at about 110° C. The weighing procedure after treatment was the same as before. The same flasks were then subjected to a second treatment for 6 hours, and in some instances to a third.

The Vycor flasks were not received until after the tests had been started. The tests of this ware were, therefore, not made simultaneously with those of any of the other three brands. However, since the conditions of test were duplicated rather closely, it is believed that the results can be safely compared with those for the other wares.

The reagents used, besides distilled water, can be divided into three groups: Strongly acid, strongly alkaline, and nearly neutral. The results obtained with the three groups of reagents are shown in tables 4, 5, and 6. For convenience, the results obtained with water are included with those of the acid group.

In order to show the extent of the variations in results obtained with different flasks, and during the successive periods of test, all of the individual results are tabulated, together with the averages for each flask and for each period of test. All the results obtained are reported. Only two results (for Vycor flasks treated with water) have been rejected in computing averages. These two were rejected because they deviate excessively from the average of the others in the same series.

Since the average deviation of the 45 trial weighings (from the averages of each of the nine groups of five weighings shown in table 3) is 0.05 mg, and since two weighings are involved in each test of a flask, differences in individual results in tables 4, 5, and 6, greater than 0.1 mg can be regarded as significant, in general. However, since the experimental work was not planned specifically with the object of detecting differences in chemical resistance between individual specimens of glassware, it is believed that more attention should be given to the average results for each group of flasks. Again, although significant differences seem to occur in some instances between the results for the successive periods of treatment, their failure to occur more generally makes them hard to explain. In the graphic presentation of the results, in figures 1, 2, and 3, only the grand averages are shown.

In comparing results obtained with different reagents, account should be taken of the occasional variations in the testing procedure or in the length of the periods of test.

1. ACID REAGENTS AND WATER

The numbers of the following explanatory notes correspond to the numbers attached to each group of data in table 4 and figure 1:

1. Distilled water.
2. Approximately normal sulfuric acid.
3. Approximately normal phosphoric acid (one-third molar).
4. Approximately 6 *N* ("constant-boiling") hydrochloric acid. About midway of the 6-hour period of boiling the flasks were replenished with acid of the same strength instead of with water.

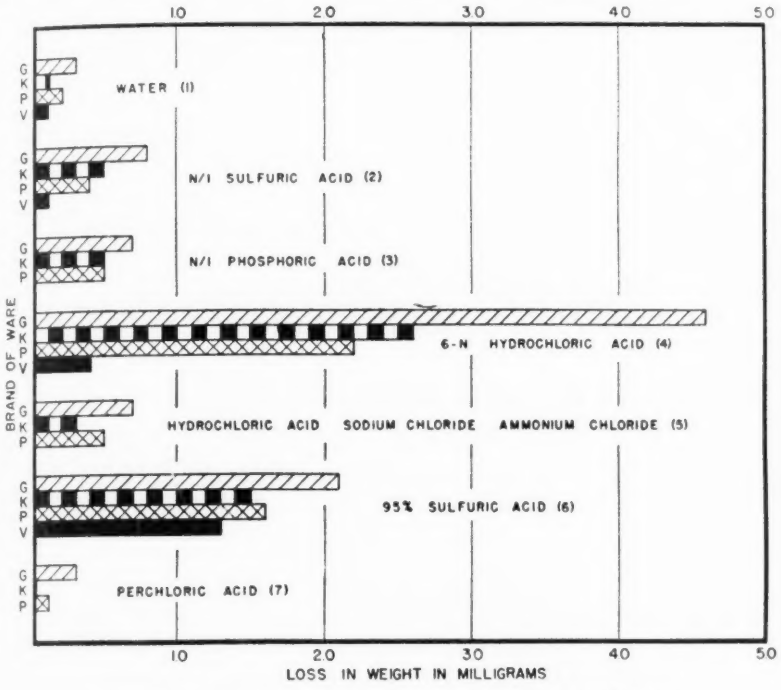

FIGURE 1.—*Comparative resistance to acid reagents and water.*
Average loss in weight, in milligrams, per flask per 6-hour period of exposure.

5. A solution containing 50 ml of concentrated hydrochloric acid, 50 g of sodium chloride, and 50 g of ammonium chloride, in 1 liter.

6. Sulfuric acid, 95 percent. Fifty ml was used instead of the usual 200 ml, and the flasks were heated on a gas hot plate. Since the area of glass exposed to the boiling acid was not the same as with most of the other reagents, the results are not directly comparable with those obtained with the others. No replenishment of acid was necessary.

7. Perchloric acid. Fifty ml of 60-percent acid was used for the first period of 6 hours. The electric hot plate used did not supply enough heat to keep the acid boiling, but much of the acid evaporated. For the second period, 100 ml of acid was used. The flasks were heated on a gas hot plate to keep the acid boiling gently. No acid was added during either of the 6-hour periods.

TABLE 4.—*Observed losses* [a] *in weight (milligrams) of flasks exposed to acid reagents and water*

Glasbake, periods				Kimble, periods				Pyrex, periods				Vycor, periods			
1	2	3	Average	1	2	3	Average	1	2	3	Average	1	2	3	Average
1. WATER															
0.3	0.5	0.0	0.2_7	0.0	0.1	0.3	0.1_3	0.2	0.3	0.2	0.2_3	0.2	[b]0.9	0.2	0.2_0
.5	.5	.0	$.3_3$	+.1	.3	.2	$.1_3$	.3	.1	.0	$.1_3$	.1	[b]1.0	.2	$.1_5$
.3	.5	.5	$.4_3$	.1	.3	.1	$.1_7$	.1	.3	.3	$.2_3$	.4	0.5	.0	$.3_0$
------	------	------	------	------	------	------	------	------	------	------	------	.0	.0	------	$.0_0$
------	------	------	------	------	------	------	------	------	------	------	------	.2	.0	------	$.1_0$
------	------	------	------	------	------	------	------	------	------	------	------	.1	.0	------	$.0_5$
Avg.... 0.3_7	0.5_0	0.1_7	0.3_4	0.0_0	0.2_3	0.2_0	0.1_4	0.2_0	0.2_3	0.1_7	0.2_0	0.1_7	0.1_2	0.1_3	0.1_4
2. 1 *N* SULFURIC ACID															
1.1	0.9	0.9	0.9_7	0.6	0.3	0.6	0.5_0	0.7	0.4	0.3	0.4_7	0.0	0.2	------	0.1_0
1.1	1.1	1.0	1.0_7	.6	.4	.6	$.5_3$	.6	.1	.5	$.4_0$	.0	.2	------	$.1_0$
1.1	0.4	0.8	0.7_7	.5	.5	.6	$.5_3$	.6	.4	.1	$.3_7$	.3	+.1	------	$.1_0$
1.3	.7	.8	$.9_3$	.8	.4	.5	$.5_7$	.9	.3	.1	$.4_3$	------	------	------	------
0.9	.3	.9	$.7_0$	.6	.1	.6	$.4_3$	.9	.0	.3	$.4_0$	------	------	------	------
.8	.7	.2	$.5_7$	.6	.5	.3	$.4_7$	.5	.1	.2	$.2_7$	------	------	------	------
Avg.... 1.0_8	0.6_8	0.7_7	0.8_3	0.6_2	0.3_7	0.5_3	0.5_1	0.7_0	0.2_2	0.2_5	0.3_9	0.1_0	0.1_0	------	0.1_0

3. 1 *N* PHOSPHORIC ACID

315285—41——6

3. 1 *N* PHOSPHORIC ACID

	0.9	0.5	.....	0.7_0	0.7	0.5	.....	0.6_0	0.6	0.4	.....	0.5_0	.....	.....	.....	.....
	.9	.4	.....	$.6_5$	.3	.3	.....	$.3_0$	.7	.2	.....	$.4_5$	.....	.....	.....	.....
	.9	.5	.....	$.7_0$	.7	.6	.....	$.6_5$	.6	.5	.....	$.5_5$	.....	.....	.....	.....
Avg	0.9_0	0.4_7	.....	0.6_8	0.5_7	0.4_7	.....	0.5_2	0.6_3	0.3_7	.....	0.5_0	.....	.....	.....	.....

4. CONSTANT-BOILING HYDROCHLORIC ACID

	4.1	5.0	.....	4.5_5	2.4	2.9	.....	2.6_5	2.3	2.3	.....	2.3_0	0.5	0.2	.....	0.3_5
	4.7	4.8	.....	4.7_5	2.5	2.5	.....	2.5_0	2.1	2.2	.....	2.1_5	.5	.3	.....	$.4_0$
	4.1	4.7	.....	4.4_0	2.3	2.8	.....	2.5_5	2.4	2.0	.....	2.2_0	.6	.3	.....	$.4_5$
Avg	4.3_0	4.8_3	.....	4.5_7	2.4_0	2.7_3	.....	2.5_7	2.2_7	2.1_7	.....	2.2_2	0.5_3	0.2_7	.....	0.4_0

5. HYDROCHLORIC ACID-SODIUM CHLORIDE-AMMONIUM CHLORIDE

	0.7	0.7	.....	0.7_0	0.6	0.3	.....	0.4_5	0.5	0.2	.....	0.3_5	.....	.....	.....	.....
	1.1	.4	.....	$.7_5$	.2	.2	.....	$.2_0$	1.0	.2	.....	$.6_0$	.....	.....	.....	.....
	0.7	.7	.....	$.7_0$	.4	.3	.....	$.3_5$	0.6	.3	.....	$.4_5$	.....	.....	.....	.....
Avg	0.8_3	0.6_0	.....	0.7_2	0.4_0	0.2_7	.....	0.3_3	0.7_0	0.2_3	.....	0.4_7	.....	.....	.....	.....

6. CONCENTRATED SULFURIC ACID

	1.1	1.3	1.6	1.3_3	1.0	0.9	1.9	1.2_7	1.2	2.8	1.1	1.7_0	0.9	1.1	1.4	[c]1.1_3
	1.1	2.1	1.0	1.4_0	1.0	1.6	1.3	1.3_0	0.8	2.2	1.0	1.3_3	.9	2.0	1.5	1.4_7
	2.1	4.9	4.1	3.7_0	1.0	3.2	1.3	1.8_3	1.5	2.0	2.2	1.9_0	1.1	1.0	1.5	1.2_0
Avg	1.4_3	2.7_7	2.2_3	2.1_4	1.0_0	1.9_0	1.5_0	1.4_7	1.1_7	2.3_3	1.4_3	1.6_4	0.9_7	1.3_7	1.4_7	1.2_7

[a] Plus sign indicates gain in weight.
[b] This observation rejected in computing averages.
[c] The low expansivity of Vycor glass and its high softening point suggested that it might be suitable as a container for pyrosulfate fusions. Fifty grams of potassium pyrosulfate was kept fused for 6 hours in each of 3 Vycor flasks by heating them over gas burners. The temperature was not measured or closely controlled. The area exposed in each flask was about 50 cm.[2] The losses in weight ranged from 2 to 5 mg.

TABLE 4.—*Observed losses*[a] *in weight (milligrams) of flasks exposed to acid reagents and water*—Continued

Glasbake, periods				Kimble, periods				Pyrex, periods				Vycor, periods			
1	2	3	Average	1	2	3	Average	1	2	3	Average	1	2	3	Average
7. PERCHLORIC ACID															
0.5	+0.1	-------	0.2_0	0.1	0.0	-------	0.0_5	0.3	+0.3	-------	0.0_0	------	------	------	------
.1	+.1	-------	$.0_0$	.0	.0	-------	$.0_0$	.3	+.1	-------	$.1_0$	------	------	------	------
1.3	.0	-------	$.6_5$	.2	+.2	-------	$.0_0$	.3	+.1	-------	$.1_0$	------	------	------	------
Avg---- 0.6	+0.0	-------	0.2_8	0.1_0	+0.0	-------	0.0_2	0.3_0	+0.1	-------	0.0_7	------	------	------	------

[a] Plus sign indicates gain in weight.

2. ALKALINE REAGENTS

The numbers of the following explanatory notes correspond to the numbers attached to each group of data in table 5 and figure 2:

8. Twentieth-normal sodium hydroxide.
9. Half-normal sodium hydroxide.
10. Half-normal potassium hydroxide.
11. Half-normal sodium carbonate.
12. Half-normal potassium hydroxide in 95-percent alcohol. When this solution was used the flasks were connected with water-cooled

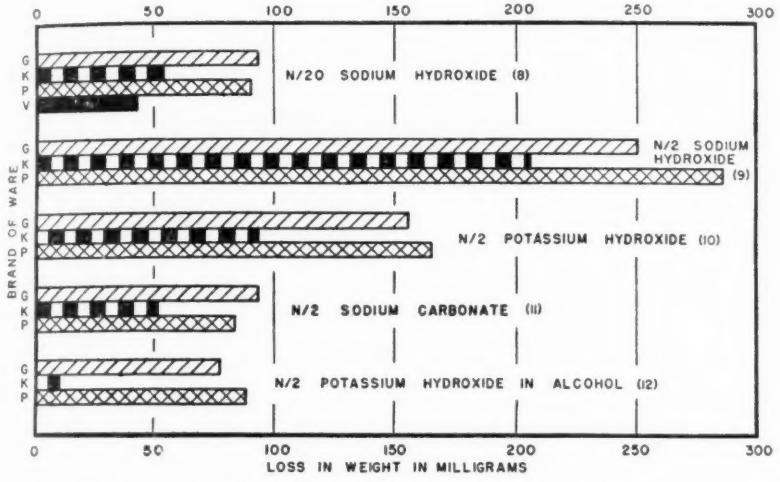

FIGURE 2.—*Comparative resistance to alkaline reagents.*

Average loss in weight, in milligrams, per flask per 6-hour period of exposure.
For 0.5 *N* potassium hydroxide in alcohol the loss in weight shown is six times the average hourly loss reported in table 5.

reflux condensers, by means of rubber stoppers. The first period was 1 hour and the second 2 hours, instead of the usual two 6-hour periods. The object of this departure from the usual procedure was to simulate actual conditions under which alcoholic potash solutions are frequently used.

13. A solution containing, at the outset, 100 ml of ammonium hydroxide (about 28 percent of NH_3) and 100 g of ammonium chloride in 1 liter. This solution was boiled in the usual way and was replenished with water. These results are not shown in figure 2.

14. Ammonium hydroxide, about 28 percent of NH_3. This reagent was used at room temperature. The flasks were closed with rubber stoppers. The first period was 8 days and the second 34 days. These results are not shown in figure 2.

TABLE 5.—*Observed losses in weight (milligrams) of flasks exposed to alkaline reagents*

	Glasbake, periods			Kimble, periods			Pyrex, periods			Vycor, periods		
	1	2	Average	1	2	Average	1	2	Average	1	2	Average
					8. 0.05 *N* SODIUM HYDROXIDE							
	90. 4	95. 6	93. 0	55. 2	59. 4	57. 3	88. 7	94. 2	91. 4	41. 0	49. 6	45. 3
	91. 8	98. 9	95. 4	53. 5	52. 5	53. 0	86. 9	93. 5	90. 2	39. 1	46. 9	43. 0
	91. 5	96. 6	94. 0	55. 4	55. 7	55. 6	88. 8	93. 4	91. 1	36. 5	46. 9	41. 7
Avg	91. 2	97. 0	94. 1	54. 7	55. 9	55. 3	88. 1	93. 7	90. 9	38. 9	47. 8	43. 3
					9. 0.5 *N* SODIUM HYDROXIDE							
	247. 9	257. 6	252. 8	172. 7	177. 9	175. 3	282. 2	286. 9	284. 6	----------	----------	----------
	241. 2	251. 0	246. 1	169. 5	157. 8	163. 6	305. 3	286. 4	295. 8	----------	----------	----------
	257. 0	252. 6	254. 8	176. 1	183. 3	179. 7	280. 5	279. 5	280. 0	----------	----------	----------
Avg	248. 7	253. 7	251. 2	172. 8	173. 0	172. 9	289. 3	284. 3	286. 8	----------	----------	----------
					10. 0.5 *N* POTASSIUM HYDROXIDE •							
	161. 1	153. 6	157. 4	94. 3	94. 9	94. 6	174. 7	162. 2	168. 4	----------	----------	----------
	158. 9	149. 7	154. 3	92. 5	92. 6	92. 6	170. 6	158. 8	164. 7	----------	----------	----------
	159. 7	152. 5	156. 1	93. 8	93. 6	93. 7	168. 9	159. 8	164. 4	----------	----------	----------
Avg	159. 9	151. 9	155. 9	93. 5	93. 7	93. 6	171. 4	160. 3	165. 8	----------	----------	----------

11. 0.5 *N* SODIUM CARBONATE

	89.4	92.5	91.0	51.5	52.5	52.0	85.7	87.3	86.5		
	96.4	98.8	97.6	53.0	54.5	53.8	81.4	83.5	82.4		
	91.6	96.2	93.9	53.9	53.8	53.8	80.5	86.3	83.4		
Avg	92.5	95.8	94.2	52.8	53.6	53.2	82.5	85.7	84.1		

12. 0.5 *N* POTASSIUM HYDROXIDE IN ALCOHOL [b]

	11.2	27.6	12.9	2.2	2.8	1.7	13.7	29.1	14.3		
	14.2	25.5	13.2	2.0	3.9	2.0	15.4	29.6	15.0		
	13.9	24.4	12.8	1.6	3.4	1.7	15.8	30.5	15.4		
Avg	13.1	25.8	13.0	1.9	3.4	1.8	15.0	29.7	14.9		

13. 10 PERCENT OF AMMONIUM CHLORIDE IN 3 PERCENT AMMONIUM HYDROXIDE

	1.9	2.2	2.0	0.9	1.5	1.2	1.2	1.4	1.3		
	2.6	1.7	2.2	0.7	0.9	0.8	1.3	1.4	1.4		
	2.8	1.5	2.2	1.1	1.4	1.2	1.9	0.9	1.4		
Avg	2.4	1.8	2.1	0.9	1.3	1.1	1.5	1.2	1.4		

14. CONCENTRATED AMMONIUM HYDROXIDE AT ROOM TEMPERATURE [c]

	2.1	1.5		1.2	1.0		1.2	1.1			
	1.3	1.7		1.0	0.9		0.3	1.3			
	1.2	1.8		0.9	0.7		0.4	1.4			
Avg	1.5	1.7		1.0	0.9		0.6	1.3			

[a] Arsenic was determined (by J.A. Scherrer) in the potassium hydroxide solution taken from 2 of each of the 3 brands of flasks after the first 6-hour period of attack. The results, in milligrams of arsenic removed from each flask, are as follows: Glasbake—0.14, 0.16; Kimble—0.06, 0.07; Pyrex—not detected (less than 0.004 mg).

[b] The first period was for 1 hour; the second period was for 2 hours. The average per period and the grand average are per hour.

[c] The first period was for 8 days; the second period was for 34 days.

3. NEARLY NEUTRAL REAGENTS

This group of reagents was made up chiefly of 5-percent solutions of sodium chloride (actually 50 g of NaCl in 1 liter of solution) adjusted to selected points on the pH scale by means of mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate. The effect of nearly neutral salt solutions was studied in some detail after it was observed that an unbuffered 5-percent solution of sodium chloride caused a pronounced attack of all the glasses (although in

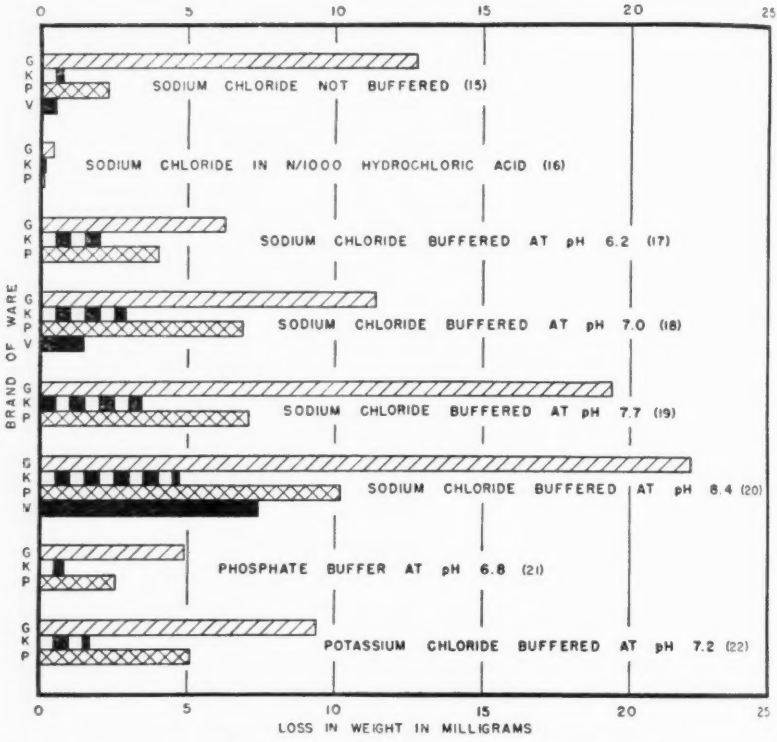
0
5
10
15
20
25
SODIUM CHLORIDE NOT BUFFERED (15)
SODIUM CHLORIDE IN N/1000 HYDROCHLORIC ACID (16)
SODIUM CHLORIDE BUFFERED AT pH 6.2 (17)
SODIUM CHLORIDE BUFFERED AT pH 7.0 (18)
SODIUM CHLORIDE BUFFERED AT pH 7.7 (19)
SODIUM CHLORIDE BUFFERED AT pH 8.4 (20)
PHOSPHATE BUFFER AT pH 6.8 (21)
POTASSIUM CHLORIDE BUFFERED AT pH 7.2 (22)
G K P V
G K P
BRAND OF WARE
LOSS IN WEIGHT IN MILLIGRAMS

FIGURE 3.—*Comparative resistance to nearly neutral reagents.*

Average loss in weight, in milligrams, per flask per 6-hour period of exposure.

varying degrees). The indicated pH is that of the solution at the beginning of the test period, at room temperature. The approximately neutral solutions used were as follows. The numbers of the paragraphs correspond to the numbers attached to the several groups of data in table 6 and figure 3.

15. Sodium chloride, 5-percent, not buffered. The solution was slightly acid at the beginning of the test period, but the contents of the flasks were slightly alkaline at the end of the period, especially in the group which showed the greatest attack. (See footnote b, table 6.)

16. Sodium chloride, 5-percent, in 0.001 *N* hydrochloric acid. All the flasks were so slightly attacked by this reagent that they were used again with the next one. This is the only instance in which any flasks were used for tests with more than one reagent.

17. Sodium chloride, 5-percent, buffered at pH 6.2. This solution contained, in addition to the sodium chloride, 10.85 g of $Na_2HPO_4.12H_2O$ and 4.55 g of KH_2PO_4, in 1 liter.

18. Sodium chloride, 5-percent, buffered at pH 7.0. In addition to the sodium chloride, the solution contained 19.0 g of $Na_2HPO_4.12H_2O$ and 1.15 g of KH_2PO_4, in 1 liter.

19. Sodium chloride, 5-percent, buffered at pH 7.7. The buffer-salt concentrations were 33 g of $Na_2HPO_4.12H_2O$ and 0.25 g of KH_2PO_4, in 1 liter.

20. Sodium chloride, 5-percent, buffered at pH 8.4. The buffer salt concentration was 33 g of $Na_2HPO_4.12H_2O$, in 1 liter.

21. Buffer solution, at pH 6.8, without sodium chloride. The solution contained 10.85 g of $Na_2HPO_4.12H_2O$ and 4.55 g of KH_2PO_4, in 1 liter. The results may be compared with those of Nos. 17 and 18 to show the marked effect of sodium chloride.

22. Potassium chloride, 7-percent (70 g in 1 liter), buffered at pH 7.2. The buffer salt concentrations were 18.5 g of $Na_2HPO_4.12H_2O$ and 1.15 g of KH_2PO_4, in 1 liter. This solution contained approximately the same molar concentrations of salts as No. 18 and was at nearly the same pH. The two sets of results show a marked difference between the effect of sodium and potassium chloride on the three glasses.

TABLE 6.—*Observed losses* [a] *in weight (milligrams) of flasks exposed to nearly neutral reagents*

Glasbake, periods				Kimble, periods				Pyrex, periods				Vycor, periods			
1	2	3	Average	1	2	3	Average	1	2	3	Average	1	2	3	Average
15. 5 PERCENT SODIUM CHLORIDE SOLUTION, NOT BUFFERED [b]															
16.6	13.0	15.7	15.1$_0$	0.6	0.8	0.7	0.7$_0$	4.4	1.2	1.4	2.3$_3$	0.2	1.2	0.0	0.4$_7$
10.6	6.5	7.9	8.3$_3$	.7	.3	1.0	.6$_7$	3.8	1.2	1.6	2.2$_0$	.0	1.0	+.1	.3$_0$
15.8	12.1	16.9	14.9$_2$	.7	.6	0.6	.6$_3$	3.4	1.4	1.7	2.1$_7$	.2	1.4	.4	.6$_7$
Avg---14.3$_3$	10.5$_3$	13.5$_0$	12.7$_9$	0.6$_7$	0.5$_7$	0.7$_7$	0.6$_7$	3.8$_7$	1.2$_7$	1.5$_7$	2.2$_3$	0.1$_3$	1.2$_0$	0.1$_0$	0.4$_8$
16. 5 PERCENT OF SODIUM CHLORIDE IN 0.001 *N* HYDROCHLORIC ACID															
0.4	0.2	-------	0.3$_0$	0.0	0.1	-------	0.0$_5$	0.2	0.2	-------	0.2$_0$	-------	-------	-------	-------
.7	.1	-------	.4$_0$	.1	.0	-------	.0$_5$	.1	.0	-------	.0$_5$	-------	-------	-------	-------
.6	.4	-------	.5$_0$	+.1	.1	-------	.0$_0$	.0	.1	-------	.0$_5$	-------	-------	-------	-------
Avg---0.5$_7$	0.2$_3$	-------	0.4$_0$	0.0$_0$	0.0$_7$	-------	0.0$_3$	0.1$_0$	0.1$_0$	-------	0.1$_0$	-------	-------	-------	-------
17. 5 PERCENT SODIUM CHLORIDE SOLUTION BUFFERED AT pH 6.2															
4.6	7.3	-------	5.9$_5$	2.1	1.8	-------	1.9$_5$	4.0	4.2	-------	4.1$_0$	-------	-------	-------	-------
5.7	8.4	-------	7.0$_5$	2.1	1.7	-------	1.9$_0$	4.5	3.8	-------	4.1$_5$	-------	-------	-------	-------
4.9	7.1	-------	6.0$_0$	2.1	1.9	-------	2.0$_0$	4.0	3.6	-------	3.8$_0$	-------	-------	-------	-------
Avg---5.0$_7$	7.6$_0$	-------	6.3$_3$	2.1$_0$	1.8$_0$	-------	1.9$_5$	4.1$_7$	3.8$_7$	-------	4.0$_2$	-------	-------	-------	-------

18. 5 PERCENT SODIUM CHLORIDE SOLUTION BUFFERED AT pH 7.0

12.5	13.3	-------	12.9$_0$	2.5	3.4	-------	2.9$_5$	7.0	6.9	-------	6.9$_5$	1.1	1.5	-------	1.3$_0$
10.6	9.6	-------	10.1$_0$	2.7	3.3	-------	3.0$_0$	8.5	6.1	-------	7.3$_0$	1.5	1.5	-------	1.5$_0$
11.4	11.4	-------	11.4$_0$	2.5	2.8	-------	2.6$_5$	7.4	5.5	-------	6.4$_5$	1.2	1.6	-------	1.4$_0$
Avg---11.5$_0$	11.4$_3$	-------	11.4$_7$	2.5$_7$	3.1$_7$	-------	2.8$_7$	7.6$_3$	6.1$_7$	-------	6.9$_0$	1.2$_7$	1.5$_3$	-------	1.4$_0$

19. 5 PERCENT SODIUM CHLORIDE SOLUTION BUFFERED AT pH 7.7

15.9	17.2	-------	16.5$_5$	2.5	4.4	-------	3.4$_5$	6.8	7.2	-------	7.0$_0$	-------	-------	-------	-------
19.2	25.2	-------	22.2$_0$	2.7	3.4	-------	3.0$_5$	6.6	7.3	-------	6.9$_5$	-------	-------	-------	-------
16.0	22.8	-------	19.4$_0$	2.8	3.6	-------	3.2$_0$	7.1	7.4	-------	7.2$_5$	-------	-------	-------	-------
Avg---17.0$_3$	21.7$_3$	-------	19.3$_8$	2.6$_7$	3.8$_0$	-------	3.2$_3$	6.8$_3$	7.3$_0$	-------	7.0$_7$	-------	-------	-------	-------

20. 5 PERCENT SODIUM CHLORIDE SOLUTION BUFFERED AT pH 8.4

23.7	21.4	-------	22.5$_5$	4.5	4.5	-------	4.5$_0$	11.3	9.2	-------	10.2$_5$	6.2	7.6	-------	6.9$_0$
24.2	25.3	-------	24.7$_5$	5.0	4.1	-------	4.5$_5$	12.2	8.9	-------	10.5$_5$	7.2	8.1	-------	7.6$_5$
20.1	17.8	-------	18.9$_5$	5.0	5.0	-------	5.0$_0$	11.3	8.1	-------	9.7$_0$	7.6	7.6	-------	7.6$_0$
Avg---22.6$_7$	21.5$_0$	-------	22.0$_8$	4.8$_3$	4.5$_3$	-------	4.6$_8$	11.6$_0$	8.7$_3$	-------	10.1$_7$	7.0$_0$	7.7$_7$	-------	7.3$_8$

21. BUFFER SOLUTION AT pH 6.8

5.4	5.5	-------	5.4$_5$	0.8	0.9	-------	0.8$_5$	2.3	2.6	-------	2.4$_5$	-------	-------	-------	-------
4.5	4.8	-------	4.6$_5$	.5	1.0	-------	.7$_5$	2.8	2.4	-------	2.6$_0$	-------	-------	-------	-------
4.5	4.7	-------	4.6$_0$	.7	.7	-------	.7$_0$	2.9	2.5	-------	2.7$_0$	-------	-------	-------	-------
Avg---4.8$_0$	5.0$_0$	-------	4.9$_0$	0.6$_7$	0.8$_7$	-------	0.7$_7$	2.6$_7$	2.5$_0$	-------	2.5$_8$	-------	-------	-------	-------

[a] Plus sign indicates gain in weight.

[b] This solution was slightly acid (acid to methyl red) at the beginning of the treatment. At the end of the 6-hour period the solutions in the Kimble and Pyrex flasks were alkaline to methyl red but acid to phenolphthalein. That in the Glasbake flasks was alkaline to phenolphthalein.

TABLE 6.—*Observed losses in weight (milligrams) of flasks exposed to nearly neutral reagents*—Continued

Glasbake, periods				Kimble, periods				Pyrex, periods				Vycor, periods			
1	2	3	Average	1	2	3	Average	1	2	3	Average	1	2	3	Average
22. 7 PERCENT POTASSIUM CHLORIDE SOLUTION BUFFERED AT pH 7.2															
10.1	10.1	-------	10.1_0	1.6	1.7	-------	1.6_5	5.8	4.9	-------	5.3_5	------	------	------	------
9.5	8.6	-------	9.0_5	1.5	1.9	-------	1.7_0	5.7	4.4	-------	5.0_5	------	------	------	------
9.8	8.2	-------	9.0_0	1.7	1.7	-------	1.7_0	5.4	4.4	-------	4.9_0	------	------	------	------
Avg---- 9.8_0	8.9_7	-------	9.3_8	1.6_0	1.7_7	-------	1.6_8	5.6_3	4.5_7	-------	5.1_0	------	------	------	------

V. RESISTANCE TO MECHANICAL SHOCK

The resistance of the 250-ml flasks to mechanical shock was determined [9] by the method currently used for determining the resistance of chinaware to chipping. Briefly, this consisted in placing a flask firmly between two cast-iron blocks forming a 90° V, and striking the flask at its maximum diameter with the tup of a pendulum of fixed length, swinging through arcs of increasing length until the glass broke.[10] After each impact, the flask was rotated slightly so that successive blows were delivered at different points on the glass. The energy (in ft-lb) required to break the glass was computed from the weight of the tup and the distance through which it swung. Vycor flasks were not included in these tests.

The results obtained on 12 flasks of each kind are given in table 7, with the flasks arranged in order of increasing weight. The average results indicate significant differences in resistance to mechanical shock. In this respect the three wares fall in the order of their relative weights. However, there is a wide range in the individual values in each group, probably because of variations in thickness and in the amount of surface checking and scratching incident to handling.

TABLE 7.—*Resistance to mechanical shock*

Glasbake		Kimble		Pyrex	
Weight	Impact energy	Weight	Impact energy	Weight	Impact energy
g	*ft-lb*	*g*	*ft-lb*	*g*	*ft-lb*
79. 3	0. 20	57. 1	0. 20	74. 0	0. 25
81. 8	. 30	59. 2	. 10	74. 4	. 25
88. 1	. 35	59. 9	. 15	76. 2	. 21
89. 9	*. 15	60. 8	. 14	78. 9	. 23
90. 5	. 50	61. 3	. 17	79. 1	. 20
91. 2	. 55	62. 5	. 15	80. 0	. 20
91. 4	. 65	62. 6	. 15	81. 0	. 20
94. 0	. 35	63. 1	. 10	82. 2	. 30
94. 1	. 50	63. 1	. 22	83. 0	. 32
95. 2	. 40	63. 6	. 13	83. 2	. 45
95. 3	. 60	66. 3	. 15	83. 3	. 45
96. 5	. 40	66. 7	. 14	85. 0	. 45
Avg__ 90. 6	. 44	62. 2	. 15	80. 0	. 29

* Abnormal result. The break occurred at 1 of the points of support, rather than at the point of impact. This result was rejected in computing the average.

VI. RESISTANCE TO THERMAL SHOCK

Resistance to thermal shock was determined [11] by slowly heating a flask, containing 100 ml of a high-flash mineral oil, on a hot plate to a selected temperature, and then quickly immersing it to the neck in

[9] These tests were made by Donald Hubbard.

[10] A complete description of the apparatus used and its method of application is given in section F-3a and fig. 9 of Federal Specification M-C-301 for "Chinaware; Vitrified." (Superintendent of Documents, Washington, D. C., price, 10 cents.)

[11] These tests were made by Donald Hubbard.

ice water. If the flask did not break, it was heated to a higher temperature and again suddenly chilled. This was repeated with increments of 25° C until the flask cracked. Early in the tests it was noted that the average breaking temperature was higher for flasks which had been carefully removed from their wrappings and tested directly than it was for flasks which had been handled somewhat, in about the way glassware is commonly handled from the time it leaves the storeroom shelf until it has been cleaned and otherwise made ready for its first service in the laboratory. This handling involved relatively gentle contact of the flasks with one another and with the laboratory bench, which undoubtedly causes minute surface injuries, usually too slight to be visible. Accordingly, tests were made of two groups of 18 flasks of each brand (except Vycor). One group was tested directly as removed from the shipping containers and the other after the normal handling already described. The results are given in table 8. The results obtained with group *A*, flasks taken directly from their shipping containers, are probably of less significance than the others, since they represent ware in a condition which cannot be maintained in service, and since they may reflect differences in the care with which the flasks were packed for shipment. On the other hand, the results of group *B* cannot be safely regarded as representing the average condition of ware in service, since no attempt was made to learn whether the average breaking temperature decreased with prolonged or rougher handling.

TABLE 8.—*Resistance to thermal shock*

Temperature	Number of breaks					
	Glasbake		Kimble		Pyrex	
	Group *A*	Group *B*	Group *A*	Group *B*	Group *A*	Group *B*
°C						
175	0	1	0	[a] 5	0	0
200	3	4	2	7	0	0
225	3	6	6	2	0	4
250	4	5	7	2	2	6
275	5	2	3	2	3	2
300	3	------	------	------	10	4
325	------	------	------	------	3	2
Average breaking temperature	253	230	240	210	294	267

[a] The relatively large number of this group which broke at 175° suggested that a lower starting temperature should have been used. Accordingly, another set of 18 flasks was tested under the same conditions except with a starting temperature of 125° C. None of this group broke at 125° or 150°, and the average breaking temperature was 238° C.

Vycor ware was not included in these tests. Its very great resistance to thermal shock was demonstrated by heating a flask to redness and cooling it under a water tap, without its breaking.

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SPECTROPHOTOMETRIC DETERMINATION OF PRASEODYMIUM, NEODYMIUM, AND SAMARIUM

By Clement J. Rodden

ABSTRACT

Praseodymium, neodymium, and samarium, in nitrate solutions, have been determined by measuring the transmittancies of the solutions with a double-monochromator photoelectric spectrophotometer.

Spectral transmittancy curves from 350 to 1,000 mμ were obtained for lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium. The absorption band found to be most suitable for the determination of praseodymium was at 446 mμ; for neodymium, the bands at 521 and 798 mμ; and for samarium, 402 mμ. Lanthanum, cerium, and gadolinium show negligible absorption between 400 and 1,000 mμ. Europium shows a small absorption band at 396 mμ.

Transmittancy-concentration curves were obtained for the individual elements in concentrations ranging from 0.25 to 25 mg/ml. These curves show that for concentrations up to 10 mg/ml, solutions of neodymium follow Beer's law, while in concentrations greater than 10 mg/ml this law does not hold. Praseodymium and samarium solutions do not follow Beer's law under the conditions used.

Approximately 1 mg of praseodymium per 6 ml can be detected. The sensitivity of the neodymium test depends on the band used; 1.5 mg can be detected by using the 521 mμ band and 0.5 mg by using the 798 mμ band. The test for samarium is less sensitive than for the other two elements, 3 mg being the minimum detected.

Mixtures of the three elements were analyzed and also mixtures of each of the three elements with lanthanum. The mixtures varied from one containing 5.0 mg of neodymium and 200 mg of lanthanum, to one consisting of 75 mg of samarium, 75 mg of praseodymium, and 50 mg of neodymium. A weight of mixed oxides corresponding to approximately 200 mg of rare earth elements was used for each analysis. The accuracy obtained was of the order of ±3 mg.

A method is given for correcting the slight interference of each element in a mixture, and a procedure is outlined for the analysis of a mixture of the cerium group of elements obtained during the course of a mineral analysis.

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I. INTRODUCTION

The term "rare earth metals" is used to designate the elements cerium, praseodymium, neodymium, 61, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium,

and lutecium, which have the atomic numbers 58 to 71, and which are usually grouped with lanthanum in the periodic table. In most analytical work, however, scandium (at. No. 21), yttrium (at. No. 39), lanthanum (at. No. 57), and sometimes thorium (at. No. 90) are included with the rare earth metals, because they resemble the rare earths in many of their properties.

Because the rare earths are very similar in their chemical and their physical properties, the means of separating them are very limited. The analyst can separate scandium, cerium, and thorium from the others in the group. He can make use of the relative insolubility of the double alkali sulfates of lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium in a saturated solution of potassium or sodium sulfate to separate these elements (the cerium group) from the remainder (the yttrium group).[1] In this way it is possible to obtain elements near the extreme ends of the solubility series free from one another, but the division between the groups is not sharp.

The salts of most of the rare earth metals are colored and their solutions show characteristic sharp absorption bands in the visible and ultraviolet region of the spectrum.[2] The possibility of using these absorption bands as a means of determining the respective elements in mixtures has been recognized for a considerable time. Four different methods have been used for the estimation of the rare earths by means of their absorption spectra. In the oldest method, which is based on the Nessler principle, the test solution is diluted until, with a direct-vision spectroscope, the absorption intensities of suitable bands appear to equal those of a standard solution placed in juxtaposition.[3] This method has been used chiefly to determine impurities in so-called pure salts of the rare earths. Friend and Hall [4] used a modification of this method and stated that, "Whilst it is apparently impossible to determine directly with an approach to accuracy the amount of praseodymium nitrate in the presence of neodymium nitrate, the latter can readily be estimated in presence of up to 50% of the former in 4% solution."

The second method is based on finding the dilution necessary for the disappearance of characteristic absorption bands. Haas [5] determined the concentration of neodymium and of praseodymium in mixtures from the absorption spectra of the nitrates, by diluting the solutions until the neodymium band at 521 mμ (green region) could no longer be seen. The band at 480 mμ (violet region) was used for the determination of praseodymium. It was found that lanthanum did not interfere. Schumacher [6] determined praseodymium and neodymium in a samarium preparation by the same method. Yntema[7] suggested photographic recording in a similar method.

The third method is that of Delauney,[8] who plotted curves to show the relationship between the widths of the chief absorption bands in the visible spectrum and the lengths of the absorption tube. The widths of the bands obtained with solutions of known composition were compared with those of unknown composition, and on the

[1] W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, p. 437 (John Wiley & Sons, New York, N. Y., 1929).
[2] W. Prandtl and K. Scheiner, Z. anorg. allgem. Chem. **220**, 107 (1934).
[3] B. Brauner, Chem. News **77**, 161 (1898).
[4] J. N. Friend and D. A. Hall, Analyst **65**, 144 (1940).
[5] Haas, Beitr. Kenntnis Pru. Nd. Dissert. Berlin 47, 51, 54 (1920).
[6] G. Schumacher, Z. Kenntnis Samarium. Dissert. Berlin 14 (1921).
[7] L. F. Yntema, J. Am. Chem. Soc. **45**, 907 (1923).
[8] E. Delauney, Compt. rend. **185**, 354 (1927).

assumption that Beer's law applies, the concentrations of the salts giving bands of equal width were calculated from the inverse ratio of the lengths of the absorption tube. A photographic method of recording was used.

The fourth method is based on the use of the spectrophotometer and was used initially by Muthmann and Stützel.[9] Praseodymium and neodymium in mixtures were determined by using a visual spectrophotometer. The band at 521 mμ was employed for neodymium and the one at 480 mμ for praseodymium. The band at 480 mμ, however, is materially affected by neodymium and samarium, and therefore the results are somewhat in error. Partridge and Rodden [10] used filters of colored glass and gelatin to isolate certain bands corresponding to the absorption regions of neodymium, praseodymium, and samarium. A photoelectric means of recording was used. Though neodymium could be determined in mixtures of praseodymium and neodymium, the determinations of praseodymium and samarium in mixtures were not satisfactory. O. S. Plantinga [11] showed that neodymium could be determined in a mixture of praseodymium and neodymium by using a filter photometer with a photronic cell as the measuring device. In this procedure, 0.015 g of neodymium could be detected, and the deviation from the true value in most cases was of the order of 1 percent in equimolar mixtures containing up to 0.24 mole per liter of each ion. The measurements were affected by salts other than those of rare earths, and by the acidity.

In preliminary experiments in this laboratory with a filter photometer,[12] an attempt was made to isolate certain narrow bands by using solutions of rare earth salts as well as glasses containing rare earth oxides. The results were unsatisfactory and indicated the necessity of using some type of spectrophotometer. In the work reported in the present paper a spectrophotometer [13] was used to determine spectral transmittancy curves of lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium. Transmittancy-concentration curves for praseodymium, neodymium, and samarium were obtained. From these measurements it was possible to determine praseodymium, neodymium and samarium in mixtures of the three, together with lanthanum. Similar measurements have been made on the yttrium group of elements, and the results will be reported in a subsequent publication.

II. EXPERIMENTAL

1. APPARATUS

A Coleman double-monochromator spectrophotometer, model 10 S was used, equipped with a slit stated by the manufacturer to select a spectral region of 5 mμ. In this instrument the source of radiant energy is a line-coiled filament energized by a 4-cell lead storage

[9] W. Muthmann and L. Stützel, Ber. deut. chem. Ges. **32**, 2653 (1899).
[10] H. M. Partridge and C. J. Rodden. Abstracts of the Indianapolis meeting of the American Chemical Society, (March 1931).
[11] O. S. Plantinga, A Study of the Colorimetric Determination of Neodymium. Dissertation, New York University (1934).
[12] B. A. Brice, Rev. Sci. Instr. **8**, 279 (1937).
[13] The cost of a spectrophotometer has, prior to the recent introduction of certain moderately priced photoelectric spectrophotometers, generally precluded its use in the analytical laboratory.

battery of high capacity. The source remains substantially constant during the time required for the desired test. The radiant energy passes first through a diffraction grating attached to a condensing lens and next through a slit. The nearly homogeneous energy from that slit passes through a right-angled prism to which is attached a second diffraction grating which disperses the stray energy. A narrow exit slit then isolates the 5-mμ band of energy used in the measurements. This band can be selected anywhere in the range from 350 to 1,000 mμ. The homogeneous energy then passes through the absorption cell to a cesium oxide photocell. Absorption cells of two types were used: (1) Cylindrical cells of approximately 17 mm internal diameter which required 8 to 10 ml of solution; and (2) square cells with 13.08 mm between faces which required 5 to 6 ml of solution. *B* batteries supply the potential for the photocell. A dark current compensator is built into the spectrophotometer. A Coleman electrometer, type 3E, was used in conjunction with the spectrophotometer to measure the transmittancy (**T**)[14] of the solution.

The wavelength scale of the instrument was calibrated from 400 to 750 mμ, by means of rare earth glasses.[15]

2. MATERIALS

Lanthanum.—The lanthanum oxide was of unknown origin. Its emission spectrum [16] showed arsenic, in the order of 0.1 percent, as well as barium, calcium, and magnesium in the order of 0.01 percent. No other rare earth was detected. After ignition of the oxide at 1,100° C, an amount equivalent to 2.5 g of lanthanum was dissolved in nitric acid, the solution was evaporated to dryness on the steam bath, and the residue was dissolved in water and diluted to 100 ml in a volumetric flask. Other solutions of lanthanum were prepared from this solution by diluting with water.

Cerium.—The cerium nitrate used was prepared from the oxide obtained from one of the supply houses. The oxide contained 1.7 percent of impurities, which were chiefly thorium, chromium, and aluminum. No rare earths were detected. The cerium oxide was converted to sulfate, precipitated with ammonia, and, after washing, was dissolved in nitric acid. Water was then added and the solution evaporated to dryness and made up to 0.0231 g of cerium per milliliter with water.

Praseodymium.—The praseodymium oxide was obtained from the Charles James collection. Its emission spectrum showed faint traces of calcium, iron, magnesium, and silicon. The amount of lanthanum was estimated to be less than 1.0 percent and that of yttrium and cerium less than 0.01 percent each. No other rare earths were detected. The praseodymium oxide was ignited at 900° C, and an amount necessary to give 2.5 g of praseodymium, on the basis of Pr_6O_{11},[17] was dissolved in nitric acid and treated like the lanthanum preparation.

[14] The transmittancy is defined as the ratio of the transmission of a cell containing solution to that of an identical cell containing distilled water.

[15] Acknowledgment is made to H. J. Keegan, of the Photometry and Colorimetry Section of this Bureau, for the transmission measurements of these glasses, made on the General Electric recording spectrophotometer.

[16] Acknowledgment is made to B. F. Scribner and H. R. Mullin, of this Bureau, for emission-spectrum analyses of the salts used.

[17] P. H. M-P. Brinton and H. A. Pagel, J. Am. Chem. Soc. **45**, 1460 (1923).

Neodymium.—The neodymium material was purified by the author by crystallization of the double magnesium nitrate. The emission spectrum of the oxide showed less than 0.01 percent each of calcium, magnesium, and silicon. No other rare earth was detected. A solution containing 0.025 g of neodymium per milliliter was prepared in the way described under lanthanum.

Samarium.—The samarium oxide was obtained from the Charles James collection and showed calcium, iron, magnesium, and silicon in amounts less than 0.01 percent each. Europium was present, but in amount less than 0.01 percent. A solution of 0.025 g of samarium per milliliter was prepared as described for lanthanum.

Europium.—The europium oxide was obtained from the Charles James collection. Its emission spectrum showed the presence of gadolinium and samarium in the order of 0.1 percent each. A solution containing 0.0182 g of europium per milliliter was prepared in the way described under lanthanum.

Gadolinium.—The gadolinium oxide was obtained from the Charles James collection. Its emission spectrum showed the presence of europium as a major constituent. No other rare earths were detected. A solution containing 0.025 g of gadolinium (Gd+Eu) per milliliter was prepared in the way described under lanthanum.

From these master solutions, mixtures which contained different amounts of the several elements were prepared.

3. TRANSMITTANCY MEASUREMENTS

Spectral transmittancy (*ST*) curves for lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium nitrate

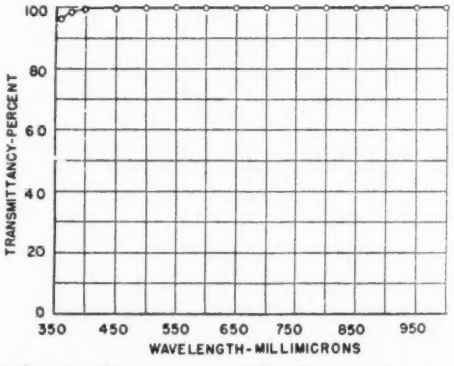

FIGURE 1.—*Spectral-transmittancy curve of lanthanum nitrate solution containing 0.25 g of lanthanum per 10 ml.*

Cylindrical cells employed.

solutions are shown in figures 1, 2, 3, 4, 5, 6, and 7. For all but lanthanum, cerium, and gadolinium, readings were made at intervals of 10 mμ, except where intense absorption bands occurred, in which case 1- to 2-mμ steps were used in order to obtain the transmittancy and wavelength at minimum transmittancy. Readings obtained for lanthanum, cerium, and gadolinium were made at the wavelengths indicated in the figures. The *ST* curve for a mixture of praseodymium, neodymium, and samarium is shown in figure 8.

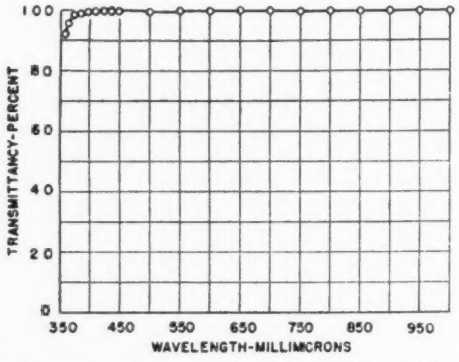

FIGURE 2.—*Spectral-transmittancy curve of cerium nitrate solution containing 0.231 g of cerium per 10 ml.*

Square cells employed.

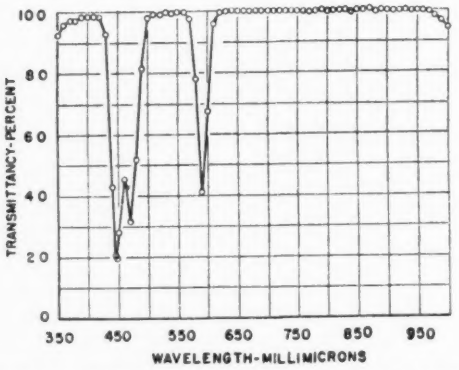

FIGURE 3.—*Spectral-transmittancy curve of praseodymium nitrate solution containing 0.25 g of praseodymium per 10 ml.*

Cylindrical cells employed.

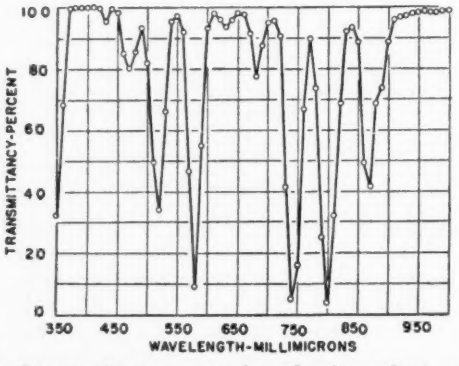

FIGURE 4.—*Spectral-transmittancy curve of neodymium nitrate solution containing 0.25 g of neodymium per 10 ml.*

Cylindrical cells employed.

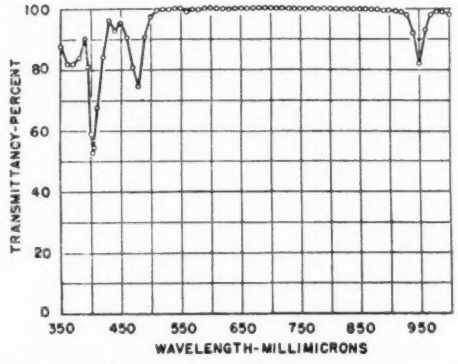

FIGURE 5.—*Spectral-transmittancy curve of samarium nitrate solution containing 0.25 g of samarium per 10 ml.*

Cylindrical cells employed.

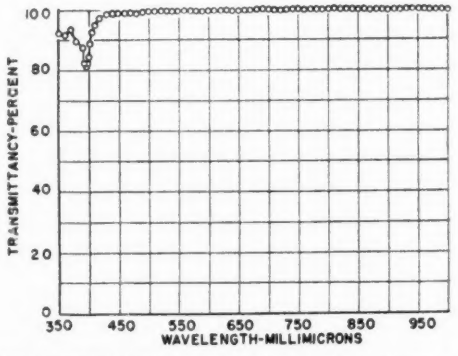

FIGURE 6.—*Spectral-transmittancy curve of europium nitrate solution containing 0.182 g of europium per 10 ml.*

Square cells employed.

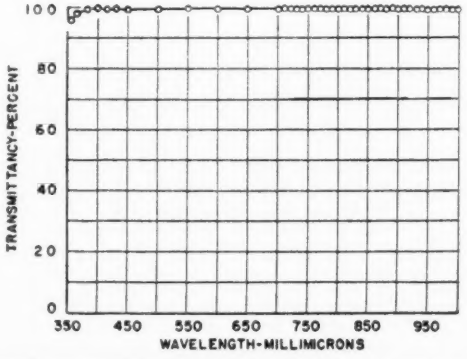

FIGURE 7.—*Spectral-transmittancy curve of gadolinium nitrate solution containing 0.25 g of gadolinium per 10 ml.*

Square cells employed.

The only band which can be used for the determination of praseodymium in mixtures is the one with minimum transmittancy at 446

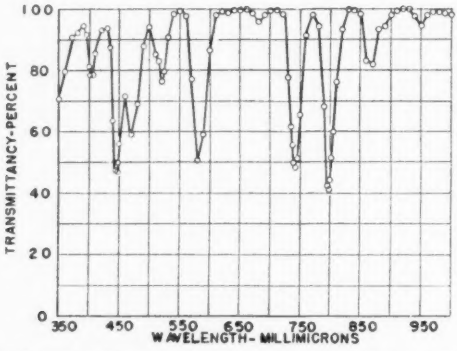

FIGURE 8.—*Spectral-transmittancy curve of a nitrate solution containing 0.050 g of neodymium, 0.075 g of praseodymium, and 0.075 g of samarium per 10 ml.*

Cylindrical cells employed.

mμ, as neodymium and samarium interfere with the use of the band at 469 mμ, and neodymium with the one at 590 mμ. As can be seen in figure 5, the band at 446 mμ is affected somewhat by samarium.

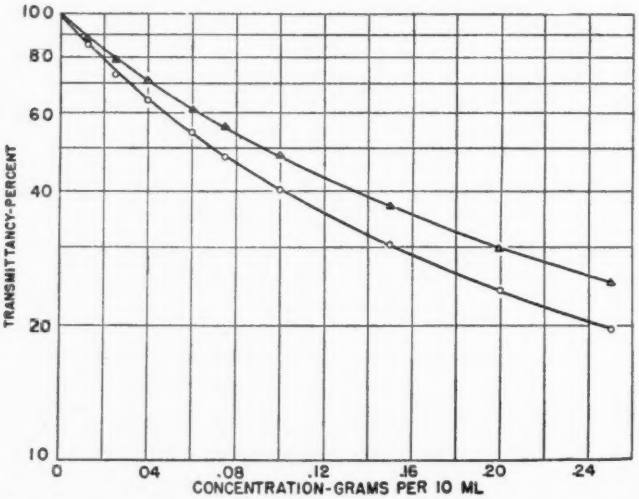

FIGURE 9.—*Transmittancy-concentration curves of praseodymium nitrate solutions at 446 mμ.*

△, Values obtained using square cells.
○, Values obtained using cylindrical cells.

The bands of neodymium nitrate at 521, 742, 798, and 870 mμ are, fortunately, free from interference by praseodymium or samarium. These bands differ considerably in amount of absorption, the one at 798 mμ absorbing the most strongly and therefore yielding the most sensitive test procedure.

The absorption band of samarium nitrate at 402 mμ is the only one which can be used for this element, because the absorption at 949 mμ is rather low and praseodymium and neodymium interfere at 479 mμ. The bands of samarium show less absorption than the other elements of the cerium group except europium, hence, samarium can be determined less precisely than neodymium and praseodymium.

Transmittancy-concentration curves for praseodymium, neodymium, and samarium were obtained with both square and cylindrical cells.

The transmittancies of praseodymium nitrate solutions were obtained at 402, 446, and 521 mμ, at concentrations ranging from 0.0125 to 0.25 g of praseodymium per 10 ml. (This material may have as high as 1 percent of lanthanum.) The results for the band at 446

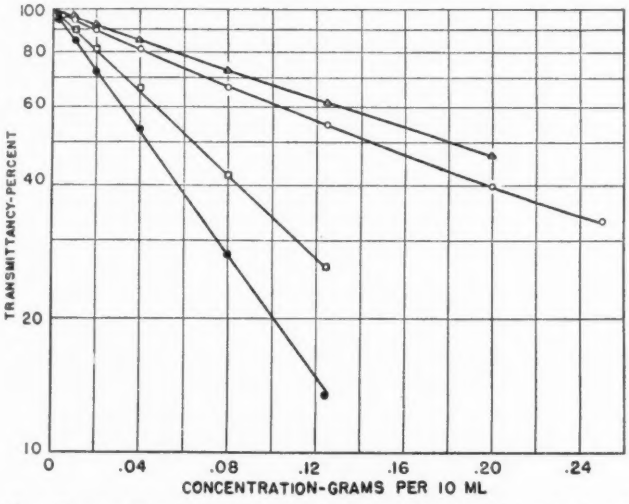

FIGURE 10.—*Transmittancy-concentration curves of neodymium nitrate solutions a the wavelengths indicated.*

△, Values obtained using square cells at 521 mμ.
○, Values obtained using cylindrical cells at 521 mμ.
□, Values obtained using cylindrical cells at 578 mμ.
●, Values obtained using cylindrical cells at 798 mμ.

mμ are shown in figure 9. The deviation from Beer's law in this case is evident. The results at 402 mμ are shown in figure 12 on an enlarged linear scale. The effect of praseodymium at 521 mμ is also indicated in this figure.

Transmittancy-concentration curves for amounts of neodymium ranging from 0.0025 to 0.25 g per 10 ml are shown in figure 10 for the 521, 578, and 798 mμ bands of neodymium nitrate. Beer's law holds closely for the 521, 578, and 798 mμ bands in concentrations up to 0.10 g per 10 ml. There is a slight deviation from Beer's law for the band at 521 mμ when the concentration increases to 0.25 g per 10 ml. The values at 402 and 446 mμ are shown on an enlarged linear scale in figure 12.

The transmittancy-concentration curves of samarium nitrate for the band at 402 mμ, for concentrations ranging from 0.025 to 0.25 g of

samarium per 10 ml, is shown in figure 11. The transmittancies at 446 and 521 mμ are shown in figure 12.

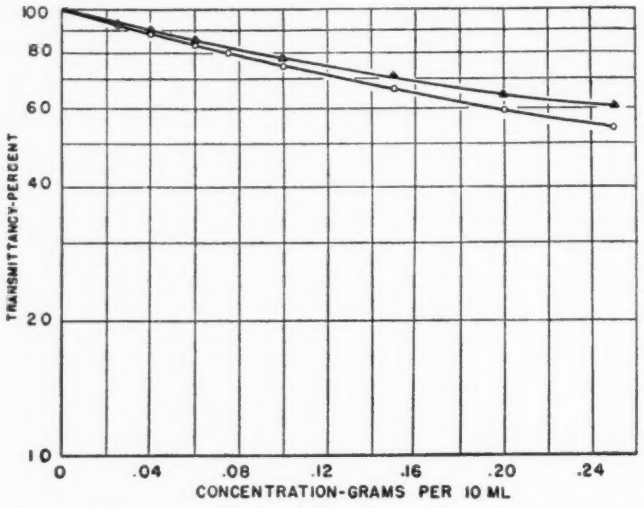

FIGURE 11.—*Transmittancy-concentration curves of samarium nitrate solution at 402 mμ.*

△, Values obtained using square cells.
○, Values obtained using cylindrical cells.

The transmittancy-concentration curves show that the amount of each rare earth element in a solution for analysis should not exceed

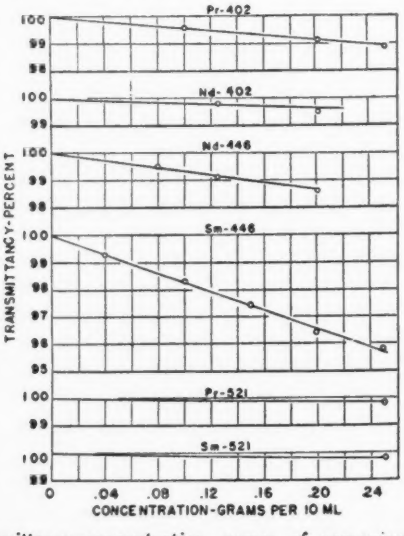

FIGURE 12.—*Transmittancy-concentration curves of samarium, neodymium, and praseodymium nitrate solutions at the wavelengths indicated, using square cells.*

approximately 0.20 g per 10 ml. This is about the maximum which can effectively be used, especially in the case of samarium, concentra-

tions of which greater than 0.20 g per 10 ml in the square cells change the transmittancy but slightly.

It will be noted from figure 12 that the presence of other rare earths will affect the transmittancy measurement of each element in question to a certain extent, and that the 446 mμ band, which is used for the praseodymium determination, may be thus affected to the greatest extent. It is possible, however, to correct for the effect of these different elements, as will be shown later. The effect of lanthanum on small amounts of other rare earths in the cerium group was studied to see if any noticeable wavelength shift in bands was observed, as was reported by Quill, Selwood, and Hopkins.[18] In the concentrations used, the shift of the bands, if present, was not sufficient to affect the results. Figure 8 shows that no noticeable shift in the wavelengths of minimum transmittancy of the bands was observed in a mixture of praseodymium, neodymium, and samarium.

III. RESULTS OBTAINED

A tabulation of the data obtained with a mixture of 0.075 g of samarium, 0.075 g of praseodymium, and 0.050 g of neodymium in a volume of 10 ml in square cells is shown in table 1.

TABLE 1.—*Illustration of the data obtained in the analysis of a solution of samarium, praseodymium, and neodymium*

1	2	3	4	5	6	7	8	
Element	Wavelength	Apparent transmittancy	Transmittancy of Pr at wavelength of col. 2, excluding 446	Transmittancy of Nd at wavelength of col. 2, excluding 521	Transmittancy of Sm at wavelength of col. 2, excluding 402	Corrected transmittancy of element listed in col. 1. Col. 3÷4×5×6	Amount of element	
							Present	Found
	mμ	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*g*	*g*
Sm	402	82.4	99.7	99.8	----------	82.8	0.075	0.075
Pr	446	53.6	----------	99.6	98.5	54.7	.075	.076
Nd	521	80.4	99.9	----------	100.0	80.5	.050	.052

The transmittancy of the solution at 402, 446, and 521 mμ is entered under column 3. From the transmittancy-concentration curves [19] of samarium, praseodymium, and neodymium, as given in figures 11, 9, and 10, it is noted that the apparent transmittancy given in column 3 corresponds to approximately 0.079 g of samarium, 0.080 g of praseodymium, and 0.054 g of neodymium per 10 ml. From figure 12, which shows the transmittancy due to samarium, praseodymium, and neodymium at the various wavelengths, are obtained the values which are entered in columns 4, 5, and 6. The transmittancy due to the element in question is then found by dividing the values in column 3 by the product of the values in columns 4, 5, and 6. This value is entered in column 7. From the transmittancy-concentration curves of figures 9, 10, and 11, the concentrations of the various elements are found and listed in column 8.

[18] L. L. Quill, P. W. Selwood, and B. S. Hopkins, J. Am. Chem. Soc. **50**, 2929 (1928).

[19] Since the transmittancy curves may vary importantly with slit-width and cell thickness, analysts should not use the data in this paper but should obtain their own standard curves.

The data in table 2 illustrate the results obtained by the method when applied to mixtures of praseodymium, neodymium, and samarium.

TABLE 2.—*Results obtained in the analysis of nitrate solutions containing varying amounts of* Pr, Nd, *and* Sm

Mixture	Concentration		
	Amount present	Amount found	
		Cylindrical cells	Square cells
	g/10 ml	*g/10 ml*	*g/10 ml*
Samarium	0.025	0.025	0.025
Neodymium	.200	.202	.198
Samarium	.200	.200	.199
Neodymium	.025	.026	.026
Neodymium	.150	.150	.150
Praseodymium	.025	.025	.026
Neodymium	.025	.028	.030
Praseodymium	.150	.151	.153
Neodymium	.050	.051	.052
Praseodymium	.075	.075	.076
Samarium	.075	.074	.075
Lanthanum	.200	Not determined	----
Praseodymium	.005	.005	.005
Lanthanum	.200	Not determined	----
Samarium	.010	.010	.012
Lanthanum	.200	Not determined	----
Neodymium	.005	.006	.006

IV. DISCUSSION

Lanthanum, cerium, and gadolinium all show the same type of general "absorption" (1–**T**) from 350 to 450 mμ. Extremely fine particles of dust, filter-paper fibers, and the like, which scatter the light at short wavelengths, may be the cause of this effect. It is recommended that all solutions used be centrifuged to remove as many particles as possible before transmittancy measurements are made.

The variation in reading transmittancy is seldom greater than ±0.2 unit on a scale of 100.0 units. The reproducibility of the wavelength setting is illustrated by the following data obtained for a solution of neodymium. Each reading represents a separate setting of the wavelength scale.

Wavelength setting	Percent transmittancy		
mμ			
729	76.8	76.7	76.6
730	69.5	69.5	69.4
731	62.7	62.9	62.9

The data in table 2 show that deviations greater than ±3 mg are usually not obtained.

The presence of 2 mg of praseodymium can be detected when the cylindrical cells are used and 1 mg with the square cells. The sensitivity of the neodymium test depends on the band chosen; 0.5 mg in 6 ml can be detected at 798 mμ. When the 521 mμ band is used, 1.5 mg of neodymium can be detected. Samarium does not give a very sensitive test, 3 mg of it in a volume of 6 ml being the smallest amount of this element which can be detected.

Europium, whose nitrate *ST* curve is shown in figure 6, seriously affects the determination of samarium. However, the amount of europium can be determined by reduction and subsequent oxidation.[20] The transmittancy indicated for samarium could then be corrected for the interference of europium by means of a transmittancy-concentration curve of europium. Gadolinium, whose nitrate *ST* curve is shown in figure 7, has no bands from 350 to 1,000 mμ, but has a slight absorption similar to that of lanthanum near 350 mμ. The *ST* curve of cerium nitrate is shown in figure 2 to indicate the effect of this element.

The applications of this spectrophotometric method in rare earth chemistry are many. The use of certain rare earths in the ceramic industry has introduced the problem of determining neodymium. As such mixtures are usually confined to members of the cerium group, a determination of neodymium can be readily made. The application of the method in following fractional crystallizations during the separation of rare earths is noteworthy. Impurities may be determined in so-called pure rare earth salts.

In a mineral analysis, the group consisting of lanthanum, cerium praseodymium, neodymium, samarium, europium, and gadolinium can be separated from the other group, but, as stated in the introduction, the separation is not sharp. However, by adding sodium sulfate until the neodymium absorption bands disappear it will be found that practically all of the cerium group is removed, contaminated somewhat by small amounts of some of the elements of the yttrium group. In the usual method of mineral analysis the cerium group is separated from the yttrium group, and cerium then determined by oxidation and titration.[21] Cerium is reported as Ce_2O_3 and the remainder of the cerium group as mixed oxides of the form R_2O_3. The total summation of the analysis of the mineral is then somewhat in error, as praseodymium forms a higher oxide whose composition in mixtures is unknown (see footnote 17).

The following procedure is suggested for the analysis of the cerium group. The rare earths are separated first from other elements by some standard procedure. The cerium group is then separated from the yttrium group as the sodium double sulfates. Cerium is separated from the other elements of the cerium group [22] and determined by oxidation and titration. As the lanthanum is determined by difference, it is necessary to treat the rare earth oxide mixture with hydrogen at 900° C to convert the black oxide of praseodymium to

[20] H. N. McCoy, J. Am. Chem. Soc. **58**, 1577 (1936).
[21] H. H. Willard and P. Young, J. Am. Chem. Soc. **50**, 1379 (1928).
[22] The author has found that this can be done quite satisfactorily by precipitating cerium as ceric hydroxide with zinc oxide. The bulk of the zinc is then separated from the rare earths by precipitating the rare earth hydroxides with a large excess of ammonia. The small amount of zinc which remains with the rare earths is removed by means of hydrogen sulfide in 0.01 *N* sulfuric acid. The rare earths are then precipitated with oxalic acid and the oxalates ignited to the oxides. This procedure will be published in a subsequent paper.

Pr_2O_3. The mixed oxides are then weighed. (Cerium is removed before the treatment with hydrogen, since it is very difficult to reduce all of the CeO_2 to Ce_2O_3.) If necessary, europium is determined by the method of McCoy (see footnote 20), but it occurs in such small amounts in minerals that its presence can ordinarily be neglected. The mixed oxides, consisting chiefly of lanthanum, praseodymium, neodymium, and samarium, are converted to nitrates by dissolving in nitric acid and evaporating to dryness on a steam bath. The nitrates are dissolved in water and diluted to a known volume. The solution is now centrifuged to remove dust particles. Praseodymium, neodymium, and samarium are then determined by measuring their transmittancies at the proper wavelengths. The equivalent amounts of the several rare earths are calculated, as described in section III, from transmittancy-concentration curves constructed from transmittancy measurements on solutions prepared from salts of high purity. Lanthanum is obtained by difference. Gadolinium has no absorption in the visible region of the spectrum and will be included in the lanthanum value.

WASHINGTON, November 20, 1940.

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CRITICAL STUDY OF THE DETERMINATION OF CARBON MONOXIDE BY COMBUSTION OVER PLATINUM IN THE PRESENCE OF EXCESS OXYGEN

By Joseph R. Branham, Martin Shepherd, and Shuford Schuhmann

ABSTRACT

This is one of a series of papers reporting direct measurements of the fundamental accuracy of methods of gas analysis.

Carbon monoxide of known purity was analyzed by the slow-combustion method. The contraction after burning, the carbon dioxide produced, and the oxygen consumed were measured. Apparatus with and without rubber connections were used. The distinct effect of the amount of liquid water within the combustion pipette and burette was measured. Analyses were performed with all gases dry, as well as saturated with respect to water vapor. The stoichiometric relationship representing ideal physical and chemical conditions is $2\,CO+O_2 \rightarrow 2\,CO_2+TC$ (where TC = total contraction after burning); the observed relationship, representing average laboratory practice by the customary method and with the usual apparatus, was $2\,CO+1.001\,O_2 \rightarrow 1.986\,CO_2+1.014$ TC. The purity of the carbon monoxide, expressed as percentage by volume, was known to be higher than 99.99. The purity determined by analysis varied from 99.13 to 101.74, depending on the measurement selected for calculation. Best results were obtained by computing CO from $TC+CO_2$; the purity so indicated was 100.01 ± 0.04. The differences between the observed relationships and the stoichiometric ones were essentially accounted for experimentally and theoretically.

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I. INTRODUCTION

One of the principal and best methods employed for the determination of carbon monoxide is combustion over hot platinum in the presence of excess oxygen—the so-called slow combustion method. The reproducibility of this method has long been known, even though infrequently disclosed. The *fundamental accuracy* of the method has not been previously known. This accuracy was measured by the simple, direct procedure of preparing carbon monoxide of high purity, measuring its purity by a method far more sensitive and accurate than the analytical method to be studied, and then analyzing this known substance by the method under investigation to observe the deviation from known fact. In addition, an explanation of this deviation has been experimentally and theoretically worked out.

II. CARBON MONOXIDE USED FOR ANALYSIS

1. PREPARATION

The carbon monoxide for this investigation was prepared by the reaction of phosphoric acid with formic acid, and was purified by fractional distillation at low temperatures in a rectifying column.

The generator used is illustrated schematically in figure 1. The various glass parts were fused directly together, or connected by ground glass joints sealed with a thermoplastic cement or a high-vacuum lubricant. The parts comprising the generator are:

A, leveling bulb containing mercury, connected by rubber nitrometer tubing to *B*.

B, reservoir containing a small amount of formic acid over mercury.

C, drop counter.

D and *E*, generating flasks containing 85 percent phosphoric acid.

F, condenser for excess water.

G, absorber filled with Ascarite.

H, condenser, with filter, immersed in liquid air.

I, *J*, and *K*, barometric mercury seals.

The stopcocks are numbered.

Since the reagents employed may be expected to yield dissolved air, and particularly nitrogen whose removal from carbon monoxide would be difficult if not impossible, the procedure was planned to remove dissolved gases prior to generating the carbon monoxide. The following steps were taken:

1. The apparatus to the left of cock 5 was evacuated through cock 4 to a pressure slightly above that of the vapor pressure of the formic acid.

2. The apparatus was filled to cock 3 with carbon dioxide through cock 1. This carbon dioxide was taken from a commercial cylinder which was about half full. Analysis of large samples of the gas indicated freedom from any significant amount of air.

3. The apparatus was evacuated and refilled with carbon dioxide four times.

4. After the fourth filling, carbon dioxide was passed for 48 hours through the apparatus to the outside, through the lower outlet of cock 3. The inlets of *D* and *E* terminated in bubbler tips of the Branham-Sperling type [1],[1] which insured intimate contact between the carbon

[1] Figures in brackets indicate the literature references at the end of this paper.

dioxide and acid, and further displacement of dissolved gases not already removed by the previous steps.

5. The phosphoric acid in both *D* and *E* was heated to 150° C, and then formic acid was admitted dropwise to *D*. The rate of flow of formic acid was adjusted by admitting mercury from *A* through the control cock, 6. The generation of carbon monoxide was immediate, and this gas was at first allowed to escape through the barometric seals, and then to fill the absorber, *G*, and escape through the seal, *K*.

6. While the reaction thus proceeded, the apparatus was thrice evacuated and refilled with the generated gas. Thereafter, the gas produced was allowed to escape through seal, *K*, for 2 hours.

7. The apparatus to the right of cock 5, of which only a condenser is shown [2], was the one used in this laboratory to purify gases by

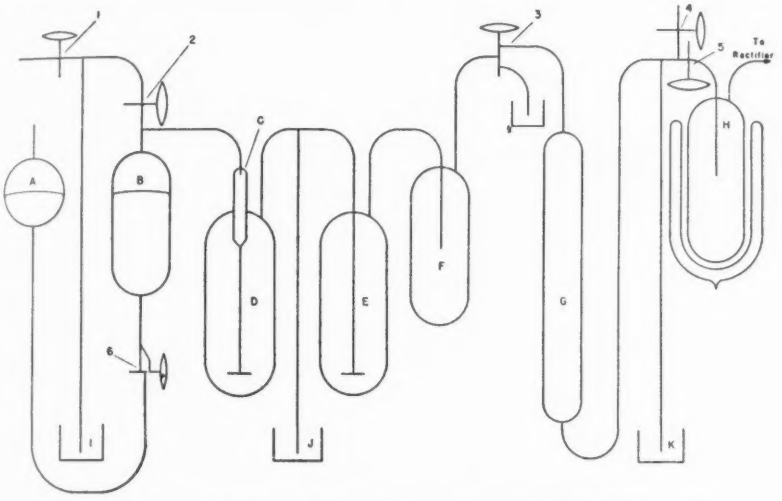

FIGURE 1.—*Flow diagram of apparatus for generating carbon monoxide.*

fractional distillation, and to determine purity by measuring the difference between the saturation pressures of an initial condensate and a final residue obtained by distillation. This apparatus was evacuated to maintain a pressure of <0.0001 mm Hg.

8. After the above operations were concluded, the carbon monoxide was passed through the condenser, *H*, and from there to evacuated receivers. The rate of flow into these receivers was adjusted so that the pressure in *H* kept the carbon monoxide at the point of incipient liquefaction. About 70 liters of gas was collected, during which time several milliliters of condensate was deposited in *H*. This step would partially remove higher boiling gases if any such were present and had escaped the Ascarite.

9. The gas collected in the receivers was then liquefied in the boiling pot of a rectifying column of the purification apparatus, and distilled at the rate of approximately 6 liters (gas) per hour under equilibrium conditions at −190° C. The first 25 liters of gaseous distillate was discarded, the apparatus was then thoroughly evacuated up to the

rectifier outlet, and the next 20 liters of gaseous distillate was collected for examination, the balance being discarded. (See methods described [2].)

2. PURITY

The purity of the distillate so obtained was measured by the method of differential saturation pressures previously reported [3]. In this test, the saturation pressure of an initial distillate was compared with that of a final residue, with no middle fraction included. The distillate and residue were obtained by rectification rather than by simple isothermal distillation. These conditions impose the severest test for purity of which this sensitive method is capable. The measurements are given in table 1.

TABLE 1.—*Measurements of the differential saturation pressure of the initial distillate and the final residue*

Measurement	Δp	Temperature
	mm Hg	° *C*
Zero reading of manometer both sides evacuated and connected	0.72 .70 .71 .70 .70	−190.9
Average	0.71 ±0.01	
Reading of manometer with initial distillate in left bulb and final residue in right bulb	0.70 .72 .74 .72	−190.9
	.74 .73 .71 .71 .70 .72 .72	−190.8
Average	0.72 ±0.01	
Zero reading of manometer repeated	0.72 .72 .72 .72	−190.6
Average	0.72	

It will be seen that no significant difference exists between the saturation pressures of the initial distillate and the final residue. Within the limit of sensitivity of the test, the carbon monoxide used in this investigation was pure.

The sensitivity of the test for this particular case may be estimated from the formula

$$\Delta x_B = \frac{\Delta_p}{p_B^\circ - p_A^\circ},$$

where Δx_B is the difference in purity between the initial distillate and final residue, expressed as the mole fraction of the impurity B; p_B° and p_A° are, respectively, the saturation pressures of the impurity, B, in its pure state and the approximately pure substance, A, in its pure state, at the temperature of the test; and Δp is the differential saturation pressure measured by the manometer. The lower-boiling impurities to be suspected are nitrogen or hydrogen; the higher-boiling

impurities are methane or higher-boiling hydrocarbons. A difference of 0.01 mm in saturation pressure would result from any one of the following differences between the impurity in the initial distillate and that in the final residue:

1. 0.00002 mole fraction of nitrogen.
2. Very much less than 0.00002 mole fraction of hydrogen.
3. 0.00001 mole fraction of methane.
4. Very much less than 0.00001 mole fraction of ethane or heavier hydrocarbons, carbon dioxide, and other higher-boiling gases.

Actually, while the measurements given do not disclose the fact, the manometer cannot ordinarily be trusted to ± 0.01 mm, but 0.03 mm is a conservative figure. This would indicate that no single impurity exceeded 0.00005 mole fraction in the carbon monoxide used and insures satisfactory purity of this gas.

3. STORAGE AND TRANSFER

The sample was transferred by liquefaction and subsequent vaporization to a carefully prepared container sealed to the purification apparatus. (For details of method, see [2].) Here it was stored over mercury. This container was sealed directly to the burette of the analytical apparatus, and means provided for alternately evacuating and flushing the sampling line with mercury and with the sample itself. Thus the identity of the sample was preserved throughout the analyses.

III. ANALYTICAL APPARATUS

The carbon monoxide was analyzed with the apparatus regularly used in this laboratory for this type of work [4]. Part of the work was done with a modified form of this apparatus, which included small tubes for desiccants and solid reagents [5]. Many of the analyses were made with all rubber connections eliminated from the apparatus. Two series were performed with a dry compensator and burette, all the gases being dried over P_2O_5 before measurement.

IV. ANALYTICAL PROCEDURE

Analyses were carefully made according to the general procedures previously set forth in considerable detail [4]. Five separate groups of analyses were performed, and in some cases the general procedures referred to were modified to fit the particular need of the group. Since these analyses will be discussed separately, any modification of general procedure will be noted with the discussion of the series involved. In general, the procedure was as follows:

1. About 60 ml of N_2 was measured and stored over the KOH or pyrogallol solution.
2. About 60 ml of oxygen was measured and stored in the combustion pipette.
3. Very close to 60 ml of CO was measured and transferred slowly (15 to 20 min) over the heated spiral of the combustion pipette. After four additional passes over the wire (15 to 20 min additional), the contraction was measured.
4. The CO_2 was removed and with the usual dilution passed into the combustion pipette to regain the small amount of this gas left in this portion of the distributor.

5. The excess O_2 was removed and with dilution passed into the KOH and combustion pipettes.

Of the various reagents we have used to determine CO_2 in the products of combustion, a saturated aqueous solution of KOH was chosen for this work. This reagent has given a good account of itself with respect to the low solubility of inert gases [6].

V. SERIES 1

(Conventional apparatus and procedure)

This series of analyses is perhaps the most noteworthy, though not the most interesting, since, from the practical viewpoint, it offers a general measure of the fundamental accuracy of the determination as ordinarily performed in the laboratory with modern apparatus and with reasonable care. The procedures employed have been previously discussed [6] and no detail need be repeated here except to state that the apparatus employed the customary rubber connections, except for the introduction of the sample; a total of 0.1 ml of water in the burette and combustion pipette was used for saturating the gases measured; and the proportion of CO_2 in the products of combustion was 0.66 of the total.

The analytical data for this series are given in table 2 under series 1. A brief explanation of this table may be given with reference to the column numbers. Columns 1, 2, and 3 give, respectively, the milliliters of total contraction (TC), carbon dioxide produced (CO_2), and oxygen consumed (O_2). These have all been reduced to the common basis of a sample of 60 ml of carbon monoxide. Thus all corresponding measurements for all analyses are directly comparable. Since these data are expressed in milliliters, the unit used in making the actual observations, any deviations greater than the expected uncertainty in the volumetric measurement (± 0.03) may be seen at a glance. Column 4 notes the gain or loss of N_2 during each analysis. Columns 5, 6, and 7 give, respectively, the percentages of CO computed from TC, CO_2, and O_2. Column 8 gives the percentage of CO computed from TC+CO_2, the most reliable combination we have found in dealing with the combustion of carbon-bearing gases. This combination automatically eliminates errors caused by loss of CO_2 in water, rubber, etc., and eliminates the effect of the deviation of CO_2 from ideality.

TABLE 2.—*Analytical data*

1	2	3	4	5	6	7	8
TC	CO_2	O_2	N_2	2TC/S	CO_2/S	$2O_2$/S	$\frac{3/2(TC+CO_2)}{S}$
Series 1. Connections made with rubber tubing. 66% of CO_2 in products. 0.1 ml of H_2O present							
ml	*ml*	*ml*	*ml*	% CO	% CO	% CO	% CO
30.40	59.62	30.29	+0.25	101.33	99.37	100.97	100.02
30.35	59.64	29.99	−.01	101.17	99.40	99.97	99.99
30.39	59.56	30.01	+.04	101.30	99.27	100.03	99.96
30.39	59.57	30.07	+.09	101.30	99.28	100.23	99.97
30.49	59.51	30.02	+.01	101.63	99.18	100.07	100.00
30.48	59.51	30.06	+.06	101.60	99.18	100.20	99.99
30.48	59.55	29.96	−.07	101.60	99.25	99.87	100.03
30.47	59.52	30.08	+.08	101.57	99.20	100.27	99.99
30.44	59.61	30.06	+.01	101.47	99.35	100.20	100.04
30.43	59.64	30.07	.00	101.43	99.40	100.23	100.08

TABLE 2.—*Analytical data*—Continued

1	2	3	4	5	6	7	8
TC	CO_2	O_2	N_2	2TC/S	CO_2/S	$2O_2$/S	$\frac{3/2(TC+CO_2)}{S}$
Series 1. Connections made with rubber tubing. 66% of CO_2 in products. 0.1 ml of H_2O present—Con.							
ml	*ml*	*ml*	*ml*	% CO	% CO	% CO	% CO
30.39	59.64	29.99	−.05	101.30	99.40	99.97	100.03
30.48	59.63	30.12	.00	101.60	99.38	100.40	100.12
30.40	59.55	29.90	−.06	101.33	99.25	99.67	99.94
30.39	59.58	30.02	+.03	101.30	99.30	100.07	99.98
30.37	59.63	29.96	−.05	101.23	99.38	99.87	100.00
30.39	59.55	30.08	+.13	101.30	99.25	100.27	99.93
30.36	59.65	30.01	.00	101.20	99.42	100.03	100.01
30.35	59.65	29.98	−.03	101.17	99.42	99.93	100.00
30.42	59.66	29.90	−.18	101.40	99.43	99.67	100.09
Avg. 30.41±.04	59.59±.05	30.03±.06	+.01±.06	101.38±.13	99.32±.08	100.10±.21	100.01±.04
Series 2. No rubber connections. 66% of CO_2 in products. 0.5 ml of H_2O present							
30.57	59.49	30.14	+0.08	101.90	99.15	100.47	100.07
30.53	59.42	29.99	+.02	101.77	99.03	99.97	99.96
30.52	59.50	30.13	+.10	101.73	99.17	100.43	100.02
30.50	59.55	30.08	+.02	101.67	99.25	100.27	100.06
30.56	59.41	30.09	+.11	101.87	99.02	100.30	99.97
30.46	59.52	29.99	.00	101.53	99.20	99.97	99.98
30.52	59.52	30.12	+.08	101.73	99.20	100.40	100.04
30.53	59.40	29.90	−.03	101.77	99.00	99.67	99.92
30.52	59.51	30.04	.00	101.73	99.18	100.13	100.03
Avg. 30.52±.02	59.48±.05	30.05±.07	+.04±.04	101.74±.07	99.13±.08	100.17±.22	100.01±.04
Series 3. No rubber connections. 66% of CO_2 in products. 0.1 ml of H_2O present							
30.35	59.62	29.96	−0.02	101.17	99.37	99.87	99.97
30.34	59.66	29.99	−.02	101.13	99.43	99.97	100.00
30.36	59.66	30.05	+.02	101.20	99.43	100.17	100.02
30.36	59.72	30.05	−.03	101.20	99.53	100.17	100.08
30.25	59.74	29.95	−.04	100.83	99.57	99.83	99.98
30.33	59.66	30.04	+.04	101.10	99.43	100.13	99.99
30.29	59.75	30.03	−.01	100.97	99.58	100.10	100.04
Avg. 30.33±.03	59.69±.04	30.01±.04	−.01±.02	101.09±.10	99.48±.07	100.03±.12	100.01±.03
Series 4. No rubber connections. 66% of CO_2 in products. No H_2O present							
30.23	59.71	30.08	+0.08	100.77	99.52	100.27	99.93
30.28	59.71	30.01	+.02	100.93	99.52	100.03	99.99
30.29	59.67	30.09	+.02	100.97	99.45	100.30	99.96
30.29	59.64	30.07	+.13	100.97	99.40	100.23	99.92
30.28	59.65	29.91	−.02	100.93	99.42	99.70	99.92
30.29	59.71	30.09	+.09	100.97	99.52	100.30	100.00
30.24	59.68	29.97	+.04	100.80	99.47	99.90	99.91
30.28	59.74	30.11	+.09	100.93	99.57	100.37	100.02
30.31	59.71	30.03	.00	101.03	99.52	100.10	100.02
30.26	59.70	30.06	+.09	100.87	99.50	100.20	99.96
Avg. 30.28±.02	59.69±.03	30.04±.05	+.04±.04	100.92±.06	99.49±.04	100.14±.17	99.96±.04
Series 5. No rubber connections. 31% of CO_2 in products. No H_2O present							
30.22	59.77	29.96	−0.04	100.73	99.62	99.70	99.99
30.22	59.78	30.06	+.03	100.73	99.63	100.20	100.00
30.27	59.74	30.01	.00	100.90	99.57	100.03	100.01
30.32	59.77	30.12	+.01	101.07	99.62	100.40	100.10
30.27	59.82	29.99	−.05	100.90	99.70	99.97	100.10
30.28	59.76	30.04	.00	100.93	99.60	100.13	100.04
30.22	59.72	29.94	.00	100.73	99.53	99.80	99.93
30.24	59.68	29.94	+.01	100.80	99.47	99.80	99.91
Avg. 30.26±.03	59.76±.03	30.00±.06	−.01±.02	100.85±.10	99.59±.05	100.00±.19	100.01±.05

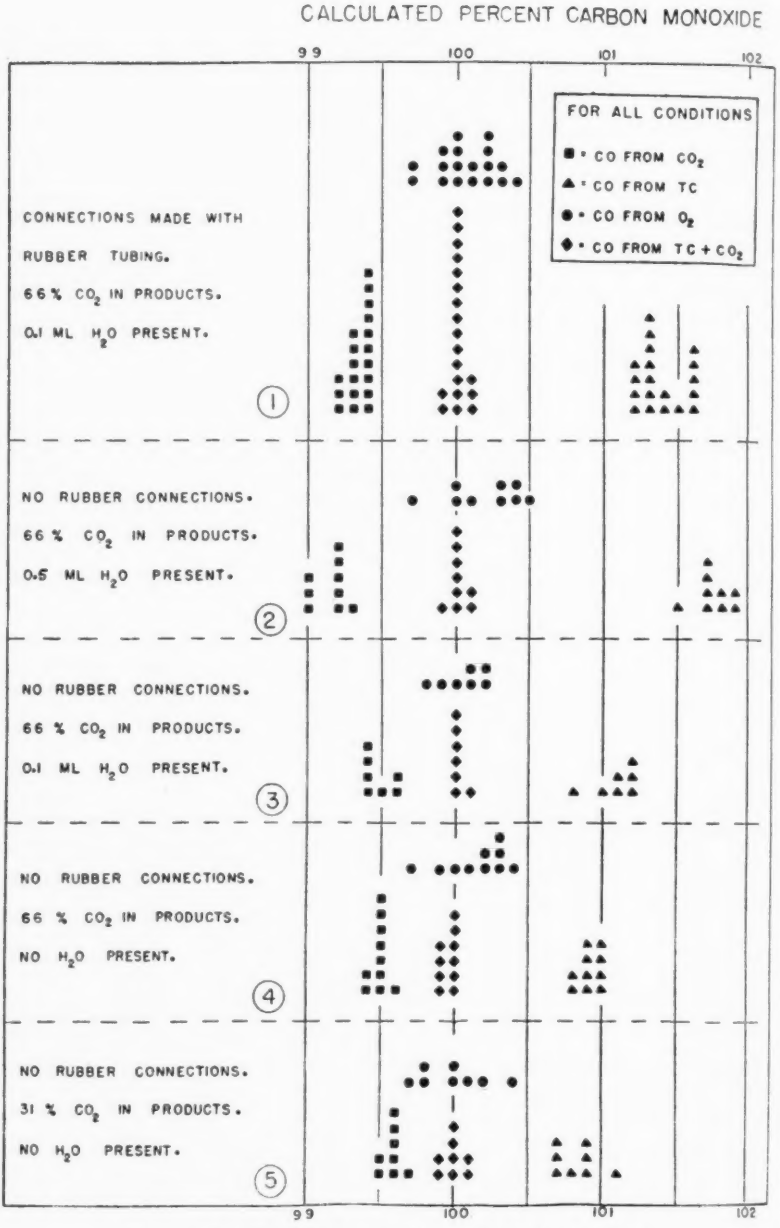

FIGURE 2.—*Graphic presentation of the analytical data.*

The data are presented graphically in figure 2, which is a frequency plot. Here the points represent percentages by volume of CO. The squares are values computed from the CO_2 produced upon combustion, the triangles are computed from the total contraction after burning, the circles are computed from the oxygen consumed, and the diamonds are computed from the more reliable combination of contraction (TC)+CO_2 produced. The values in table 2 have been rounded off to the nearest 0.1 percent in this graph.

The picture is so obvious when thus presented that discussion seems gratuitous. Again there is the usual story to be expected from a carbon-bearing gas. Carbon monoxide is too high by 1.4 percent when computed from TC, too low by 0.7 percent when computed from CO_2, too high by about 0.1 percent when computed from O_2, and so nearly correct when computed from TC+CO_2 that the limit of accuracy of the volumetric measurement will suffice to explain whatever deviation from the known composition remains. The accuracy of the analysis thus has a direct measure. The reproducibility is equally well shown at a glance. Reproducibility (expressed as average deviation from the mean) for the determinations of TC and CO_2 was about ± 0.1 percent for each of the series; the total spread was 0.5 and 0.3 percent, respectively. Reproducibility was not so good when computed from O_2, being ± 0.2 percent, with a spread of 1.3 percent. The results computed from TC+CO_2 are remarkably consistent. Indeed, for the determination of the purity of a single carbon-bearing gas in the absence of other combustible gases, the best volumetric combustion procedure would be the removal of CO_2 during the combustion, and the single measurement of the combined TC and CO_2. Unfortunately, this procedure can rarely be employed.

VI. SERIES 2 AND 3

(Conventional apparatus, but with no rubber connections. Procedure same as in series 1. Water in combustion pipette and burette: series 2, 0.5 ml; series 3, 0.1 ml)

1. EFFECT OF LIQUID WATER IN THE COMBUSTION PIPETTE

The amount of water within the burette and combustion pipette is one factor determining the accuracy of the analysis. This has been discussed before [7] but inadequately, and may be briefly reconsidered. It is necessary, of course, to keep some water within the burette if all the gas volumes are to be completely saturated and thus made comparable on this basis. (This is general practice, since dry analyses have been considered too difficult.) The amount of water used by different operators varies somewhat, but the best technique calls for a film of water on the burette walls, with no excess to obscure the mercury meniscus. If this condition is maintained, the total amount of water is, curiously enough, practically constant. If, however, free or combined hydrogen is burned, water is supplied to the combustion pipette, and accumulates therein if not regularly expelled. General practice has been to remove this condensate when it becomes troublesome—and this means that the amount of water may vary considerably from time to time—certainly over the range 0.1 to 1 ml, depending on the whim and preoccupation of the manipulator.

The physical picture with respect to this water is clear. When the gas is first burned and the condensate forms, it dissolves CO_2 from the products of combustion. The contraction measured after burning is correspondingly too high and the CO_2 equally too low. Next, after removal of the greater part of the CO_2 by absorption in KOH solution, the residue is passed into the combustion pipette to regain the small amount of this gas that has been left in the distributor connections; and at this moment the water within the combustion pipette may liberate the dissolved CO_2 which is, of course, absorbed during the final passages into the KOH solution. This leaves the water within the combustion pipette free to dissolve more CO_2 during the next combustion, a point previously ignored. If the water then accumulates, the amount of CO_2 dissolved will increase with each succeeding combustion.

This was demonstrated experimentally by introducing a known amount of water into the combustion pipette and alternately passing CO_2 and N_2 into it, measuring the alternate decrease and increase of volumes corresponding to the absorption and liberation of the CO_2. The amounts so retained and liberated corresponded with the known data for solubility under the experimental conditions. Absorption and desorption were rapid and apparently complete, since one passage of the gas (duration about 20 sec) was sufficient to give approximate equilibrium.

The effect upon the actual analysis is demonstrated experimentally in series 2 and 3. During series 2, a total of 0.5 ml of water was kept within the combustion pipette and burette. This amount was reduced to 0.1 ml during series 3. A comparison of the data shows that the expected effect was observed. The data are given in table 2. A difference of 0.21 ml of CO_2 produced is noted, with a corresponding difference of 0.19 ml in TC. This difference agrees with the value computed from the solubility of CO_2 in water at its existing partial pressure and the average temperature of the analyses: $(0.4 \times 0.8 \times 0.66 = 0.21$ ml, where 0.4 is the difference in milliliters of the amount of water, 0.8 is the solubility factor, and 0.66 the partial pressure of CO_2).

The shift in values is easily seen in figure 2. When the larger amount of water was present, the percentages computed from CO_2 and from TC are pushed farther aside from the known fact; when the smaller amount of water was used, the corresponding values are drawn in closer to the 100-percent axis. The differences between the two series are about 0.6 percent of CO computed from TC and 0.3 percent computed from CO_2. The values computed from $TC + CO_2$ are not significantly changed. The data indicate the necessity for modification of technique with respect to water accumulating in the combustion pipette. Considering the average temperature, the partial pressure of CO_2 in products of combustion, and its solubility in water, the water should be limited to 0.1 ml.

2. EFFECT OF RUBBER CONNECTIONS

Before proceeding to the next series of analyses, series 1 should be compared with series 3. The water during each series was 0.1 ml. Other conditions were comparable, except that the rubber connections used in series 1 were replaced with fused glass or cemented connections

in series 3. The loss of CO_2 through the rubber connections, an error previously discussed [8], is apparent when these analytical data are examined. Series 1 gives a higher value of CO from TC, and a lower one from CO_2, than does series 3. These differences amount to 0.3 and 0.2 percent, respectively, and correspond to a loss of 0.1 ml of CO_2 in the rubber—rather more than previous independent measurements would indicate, and probably more than is actually lost.

VII. SERIES 4

(No water and no rubber connections—all gases measured dry)

In many respects series 4 is the most interesting group of analyses performed during this work. The procedure was novel in that all gases were measured dry instead of saturated with water vapor. Thus the loss of CO_2 by solution in water was eliminated entirely. The apparatus had no rubber connections. The desiccant used was P_2O_5, small amounts of which were put on glass wool in tubes used to dry both the sample and the oxygen before they entered the burette, as well as all gases returned from reagents or the combustion pipette. Such an apparatus and the requisite procedures for using the dry burette and compensator have been described [5]. A review of this work will reveal most encouraging volumetric behavior in spite of the natural expectation that water vapor yielded from glass walls might continually interfere. Aside from the modification of apparatus and the drying of the gases, the analytical procedure was the same as for previous analyses.

The data show some decrease in the CO computed from the TC measured in this series, which was to be expected. However, contrary to expectation, there was no significant increase in the value derived from CO_2. There was no decrease in the CO calculated from the measurement of excess O_2.

During these analyses a curious thing was observed. The dry combustion pipette quickly collected what appeared to be considerable amounts of a grayish-black powder. It is true that this pipette never remains entirely clean, since iridium is deposited from the heated spiral, and mercury slowly fouls, even when transferred through the best grade of sulfur-free rubber tubing. But the fouling of the dry pipette appeared to be unmistakably worse and occurred in considerably less time than had ever been observed with the wet pipette. It is, of course, entirely possible that similar amounts of this substance are formed in the wet pipette, but are not obvious because a fluffy powder may be reduced in volume by the water, and be carried down the walls of the pipette with the moist mercury, gradually forming the dirty rings which are noticeable in the lower portions of the wet pipette.

These dry analyses presented further curious second-order effects. After the combustion, the gas was returned directly from the pipette for measurement. Thereafter, the gas was returned through the P_2O_5 to the pipette, and then back to the burette through the same desiccant. The second gas volume was usually less than the first by small amounts—0.02 to 0.05 ml. In computing the analysis, the second or the "dry" volume was taken. It is entirely possible that small amounts of water vapor were released from the heated wire and glass dome of the pipette, or crept up through the rubber tubing

connected to the bottom of the pipette. This explanation most nearly fits the physical picture involved. We were unable to measure any adsorption of CO_2 on the P_2O_5 during a set of control experiments designed to check this possible explanation.

Another puzzle developed during a second set of control experiments. Nitrogen, oxygen, or air could be repeatedly passed between the dry pipette and burette, either through the P_2O_5 or with this tube by-passed, with no significant change of volume. However, when the wire was *heated*, a small expansion was observed when nitrogen was passed into the pipette, and a small contraction was observed when oxygen (or air) was passed over the hot wire. The wet pipette gave no such effect with either gas. Extremely rigorous tests for leaks were made concurrently with these experiments, which, it will be remembered, were conducted in an apparatus without rubber connections. These expansions and contractions were of the order of magnitude of 0.05 to 0.1 ml when the two gases were exposed to the hot wire for periods of one-half to 1 hour. There was also evidence of the formation of an acid gas when either expansion or contraction was observed. Of the many explanations which occurred, none seemed satisfactory.

Whatever the cause of the small contraction observed when O_2 or air was passed over the heated spiral of the dry combustion pipette, its occurrence might explain an increased TC and O_2 and decreased CO_2 for this series. But while the CO_2 was less than expected, the TC was itself *less* than for the previous series. Again, the formation of the black substance in the dry pipette in the presence of oxygen might indicate the formation of an oxygen compound, and the O_2 consumed might indicate this. While these effects are of a second order of magnitude, they are nonetheless interesting.

The nitrogen balance for this series shows an average gain of 0.04 ml. This and the value for CO computed from $TC+CO_2$ suggest an incomplete combustion in the dry state, but we were unable to demonstrate this experimentally.

At this time it will be well to review the nitrogen balance for each of the four series of analyses already discussed. To complete the picture, the data from series 5 will be anticipated. The average nitrogen lost or gained during each series was as follows:

Series	*ml*
1	+0.01
2	+.04
3	−.01
4	+.04
5	−.01

While the amounts involved are small, the gains for series 2 and 4 are somewhat out of line. The most likely explanation for this is slightly involved, but brings out an important fact concerning the oxygen consumed during combustion. The whole picture becomes clear by correlating the following separate facts:

1. Oxygen is determined by absorption in a solution of alkaline pyrogallol. It is known from experimental work that the particular solution of pyrogallol used in this work yields no significant amount

of carbon monoxide during reaction with oxygen, provided the proportion of the oxygen is 0.2 of the whole or less, and the reaction is conducted so that little or no expended pyrogallol remains in contact with unabsorbed oxygen [9]. However, if the partial pressure of the oxygen is high, small but measurable amounts of carbon monoxide may be generated. Any carbon monoxide so produced will appear in the residue, after absorption, as so much nitrogen, and the oxygen determined will be correspondingly too low.

2. During series 1 and 3, the diluting nitrogen used with each analysis was stored over the solution of potassium hydroxide, so that it mixed with the residual gas after absorption of the carbon dioxide and before the absorption of oxygen. This lowered the partial pressure of oxygen in the gas entering the pyrogallol solution. During series 5 a like condition prevailed, since air, instead of commercial oxygen, was used for combustion in this series only. But during series 2 and 4, through an oversight, the diluting nitrogen was stored over the pyrogallol, thus making the partial pressure of oxygen in the gas originally entering this solution higher than existed during the other series. Under these circumstances, negligible amounts of carbon monoxide would be expected from the reaction of oxygen with pyrogallol in series 1, 3, and 5; but this would not be true for series 2 and 4. The data indicate that on the average about 0.04 ml of CO was generated during the absorption of excess oxygen in series 2 and 4, and that this carbon monoxide appeared as a gain in nitrogen.

3. This explanation of the nitrogen gained is consistent with determinations of carbon monoxide generated during the analysis of the commercial oxygen used for combustion during series 1 to 4, inclusive. This carbon monoxide was determined by the iodine pentoxide method and by combustion of concentrated residues from absorptions of many samples of oxygen.

While the above discussion rounds out the picture with respect to the nitrogen balance, futher consideration should be given to the small amounts of carbon monoxide sometimes generated when oxygen reacts with pyrogallol, since the measurement of oxygen consumed during the combustion will also be affected.

In general, the oxygen consumed during combustion is found by determining the excess oxygen in the products of combustion and subtracting this excess from the measured amount of oxygen originally taken. Thus the composition of the oxygen taken for combustion must be known. If air is not taken, usually commercial oxygen separated from air by rectification is used. This oxygen contains nitrogen as an impurity. Its composition is ordinarily determined by the same method used during an analysis to determine the excess oxygen in the products of combustion, that is, by absorption in alkaline pyrogallol. Since the apparent oxygen determined by this method depends upon the partial pressure of oxygen in the gas entering the pyrogallol solution, it is obvious that the determination of excess oxygen in the products of combustion may not strictly compare with the determination of oxygen in the commercial "oxygen" taken for this combustion. In other words, different amounts of carbon monoxide may be generated during these two separate but interdependent determinations. For this reason, accurate work requires the determination of generated carbon monoxide in both cases, or else

the adjustment of the partial pressures of oxygen so that they will be nearly equal during both determinations.

In the work here reported, the commercial oxygen was analyzed by absorption in pyrogallol with subsequent determination of and correction for generated carbon monoxide. In addition, analysis was made by combustion with pure hydrogen. The composition of the commercial oxygen was accordingly well established. The original analytical procedure would have eliminated significant error caused by the generation of carbon monoxide during the absorption of oxygen in the products of combustion, simply by diluting the oxygen with a sufficient amount of nitrogen. Therefore, no determination of generated carbon monoxide was made, although the failure to observe the outlined procedure in series 2 and 4 made such a determination desirable.

VIII. SERIES 5

(No water; no rubber connections; air used for the combustion instead of oxygen)

This series of analyses made use of the nearest approach to a standard gas mixture that is ordinarily available to the gas analyst—dry, CO_2-free air. The advantages gained are a definite knowledge of the amount of oxygen introduced for the combustion, a supply of diluent nitrogen without its preparation and separate measurement, and a reduction in the partial pressure of CO_2 in the products of combustion. The disadvantage is the limitation of the amount of sample which can be used, and consequently of the three measurements TC, CO_2, and O_2.

In spite of this limitation imposed on percentage volumetric accuracy, the results are pleasing with respect to TC and CO_2, both of which approached a bit nearer to the 100-percent axis which represents the known fact. The *average* of the oxygen values leaves nothing to be desired, but the reproducibility of these values is not so good. The nitrogen balance is satisfactory (−0.01 ml). This procedure has much to commend it.

IX. CORRECTION OF ANALYTICAL DATA FOR KNOWN ERRORS

Now that the analytical data have been presented, the accuracy and reproducibility of this determination made under the five sets of conditions noted are both disclosed, and the analyst and the user of his data may know about what to expect when dealing with this gas so determined. From the practical viewpoint, the analyses of series 1 offer a measure of the order of magnitude of the accuracy which may have been achieved in laboratories using modern apparatus with reasonable care, and conducting determinations in such a manner that the partial pressures of the various gases at each step of the analysis would approximate those maintained in this work.

In addition to offering this useful information, it will be well, as always, to see if something further can be done to improve these results by correcting them for known errors. If the analytical results can thus be brought into closer agreement with the known purity of the CO, the remedial measures thus indicated will be worth the using.

Assuming that the chemistry involved is above reproach, the two distinct types of error then to be expected are deviations from the ideal

gas laws, and the solution of the gases in water and rubber. These have been previously discussed [7], and data may be drawn from past experiments to make the necessary corrections involved. In addition, fresh data are offered to give, at least roughly, the order of magnitude of the deviations from ideality of the various mixtures existing during the analysis. Since these last results may be at variance with theoretical values for these deviations, the data will first be corrected for errors arising from solution in water and rubber, and then be corrected for deviations from ideality on the basis of both theoretical and approximately measured values.

In making these corrections, it will be simpler to deal in the units actually observed in the analysis—namely, milliliters of gas measured at atmospheric pressure and laboratory temperature (average 25° C). This method has the additional virtue of telling the analyst just where he stands with respect to the factor which fundamentally limits his work—volumetric accuracy. It will be seen that application of the corrections for solution of CO_2 brings the results of the five series into better agreement among themselves, and that application of appropriate corrections for deviations from the ideal gas laws brings the results into better agreement with the known facts regarding the purity of the CO.

1. CORRECTIONS FOR LOSS OF CO_2 BY SOLUTION

Corrections for solution of CO_2 in H_2O may be made for series 1, 2, and 3 on the basis that the solubility is 0.8 ml of CO_2 per ml of H_2O (at 26° C) when the pressure of CO_2 in the gas phase is 1 atmosphere. Under the conditions of the experiments in series 1, 2, and 3, in which the partial pressure of CO_2 is 0.66 atmosphere, this reduces to 0.53 ml of CO_2 per ml of H_2O. Correction for solution of CO_2 in rubber may be made for series 1 on the basis that 0.05 ml of CO_2 would be lost by this process [8] during the time of an analysis if the CO_2 were at atmospheric pressure. This corresponds to a loss of 0.03 ml of CO_2 per analysis at the partial pressure of the CO_2 in these experiments.

The observed average equations for the series, expressed in milliliters, and referred to a fixed sample of 60 ml of CO, are:

Series 1. $60\ CO+30.03\ \pm0.06\ O_2 \rightarrow 59.59\ \pm0.05\ CO_2+30.41\ \pm0.04$ TC
2. $60\ CO+30.05\ \pm0.07\ O_2 \rightarrow 59.48\ \pm0.05\ CO_2+30.52\ \pm0.02$ TC
3. $60\ CO+30.01\ \pm0.04\ O_2 \rightarrow 59.69\ \pm0.04\ CO_2+30.33\ \pm0.03$ TC
4. $60\ CO+30.04\ \pm0.05\ O_2 \rightarrow 59.69\ \pm0.03\ CO_2+30.28\ \pm0.02$ TC
5. $60\ CO+30.00\ \pm0.06\ O_2 \rightarrow 59.76\ \pm0.03\ CO_2+30.26\ \pm0.03$ TC

These equations corrected for solubility of CO_2 in water and rubber are:

Series 1. $60\ CO+30.03\ O_2 \rightarrow 59.67\ CO_2+30.33$ TC
2. $60\ CO+30.05\ O_2 \rightarrow 59.74\ CO_2+30.26$ TC
3. $60\ CO+30.01\ O_2 \rightarrow 59.74\ CO_2+30.28$ TC
4. $60\ CO+30.04\ O_2 \rightarrow 59.69\ CO_2+30.28$ TC
5. $60\ CO+30.00\ O_2 \rightarrow 59.76\ CO_2+30.26$ TC

The average equation for all five series corrected for solubility is

$$60\ CO+30.03\ O_2 \rightarrow 59.72\ CO_2+30.28\ TC.$$

The deviations of each series from this average are:

Series 1. 0.00 $O_2 \rightarrow 0.05$ $CO_2 + 0.05$ TC
2. 0.02 $O_2 \rightarrow 0.02$ $CO_2 + 0.02$ TC
3. 0.02 $O_2 \rightarrow 0.02$ $CO_2 + 0.00$ TC
4. 0.01 $O_2 \rightarrow 0.03$ $CO_2 + 0.00$ TC
5. 0.03 $O_2 \rightarrow 0.04$ $CO_2 + 0.02$ TC

The improved agreement is at once noted. CO_2 and TC for series 5 are somewhat out of line, but it will be remembered that the partial pressure of CO_2 in the products of combustion was only 0.31 for this series as against 0.66 for the other series, and correction for deviation from ideality may still remedy this.

2. CORRECTIONS FOR DEVIATION FROM IDEALITY

The next corrections in order are those dealing with deviations from the ideal gas laws. The two mixtures which will exhibit the greatest deviations during these analyses are (expressed in partial pressures) 0.66 $CO_2 + 0.34$ $[O_2 + N_2]$ (series 1 to 4, inclusive) and 0.31 $CO_2 + 0.69$ $[O_2 + N_2]$ (series 5).

Dry CO_2 and dry air were measured separately, and were mixed in such proportions that the above partial pressures were obtained. To check the measurements, two volumes of dry air were measured in like amounts. The averages of 10 such determinations of each are as follows:

1. When 60 ml of dry CO_2 was mixed with 30.9 ml of dry air, the observed expansion was 0.04 ml ± 0.01.
2. When 60 ml of dry air was mixed with 27 ml of dry CO_2, the observed expansion was 0.056, corresponding to 0.11 ± 0.02 had the sample been 60 ml of CO instead of the 30 ml necessarily used.
3. When 60 ml of air was mixed with 30 ml of air, there was no observed expansion within ± 0.01 ml.

The TC measured during the analyses will therefore be less by amounts corresponding to these expansions, and the CO_2 correspondingly greater, than if the gases had been measured separately. If we correct the equations which have already been corrected for solution of CO_2, the results are:

Series 1. 60 CO $+30.03 \pm 0.06$ $O_2 \rightarrow 59.63 \pm 0.05$ $CO_2 + 30.37 \pm 0.04$ TC
2. 60 CO $+30.05 \pm 0.07$ $O_2 \rightarrow 59.70 \pm 0.05$ $CO_2 + 30.30 \pm 0.02$ TC
3. 60 CO $+30.01 \pm 0.04$ $O_2 \rightarrow 59.70 \pm 0.04$ $CO_2 + 30.32 \pm 0.03$ TC
4. 60 CO $+30.04 \pm 0.05$ $O_2 \rightarrow 59.65 \pm 0.03$ $CO_2 + 30.32 \pm 0.02$ TC
5. 60 CO $+30.00 \pm 0.06$ $O_2 \rightarrow 59.65 \pm 0.03$ $CO_2 + 30.37 \pm 0.03$ TC

The average equation for all five of the series, taken from the above separate corrected equations, is

$$60 \text{ ml CO} + 30.03 \text{ ml } O_2 \rightarrow 59.67 \text{ ml } CO_2 + 30.34 \text{ ml TC}$$

The deviations of each series from this equation are:

Series 1. 0.00 $O_2 \rightarrow 0.04$ $CO_2 + 0.03$ O_2
2. 0.02 $O_2 \rightarrow 0.03$ $CO_2 + 0.04$ O_2
3. 0.02 $O_2 \rightarrow 0.03$ $CO_2 + 0.02$ O_2
4. 0.01 $O_2 \rightarrow 0.02$ $CO_2 + 0.02$ O_2
5. 0.03 $O_2 \rightarrow 0.02$ $CO_2 + 0.03$ O_2

This now brings the CO_2 and TC of series 5 in line with those of the other series. The differences may not represent real effects, since all of the data are now within the reproducibility of measurement.

Had the physical and chemical behavior of the analysis been perfect in all respects, the ideal stoichiometric relationship

$$60\ CO+30\ O_2 \rightarrow 60\ CO_2+30\ TC \qquad (1)$$

would have prevailed. This ideal relationship itself must be corrected for deviation of the gases from ideality, and this may be done according to values kindly supplied by C. S. Cragoe, of this Bureau. The values were calculated by Cragoe from the best available data for the average conditions prevailing during these analyses. They are believed to be good to 1 in the fourth place. The corrected equation may be written

$$(60)(0.9997)\ CO+30(0.9994)\ O_2 \rightarrow 60(0.9949)\ CO_2 \qquad (2)$$

This corresponds to

$$60\ CO+29.99\ O_2 \rightarrow 59.71\ CO_2+30.28\ TC \qquad (3)$$

The deviations of these values from the observed values corrected for solution of CO_2 are

Series 1.	$-0.04\ O_2 \rightarrow$	$+0.04\ CO_2+$	-0.05 TC
2.	$-0.06\ O_2 \rightarrow$	$+0.03\ CO_2$	-0.02 TC
3.	$-0.02\ O_2 \rightarrow$	$-0.03\ CO_2$	0.00 TC
4.	$+0.03\ O_2 \rightarrow$	$+0.02\ CO_2$	0.00 TC
5.	$-0.01\ O_2 \rightarrow$	$-0.05\ CO_2$	$+0.02$ TC

This agreement is satisfactory for nearly every measurement made during the five series of analyses, and gratifyingly so for the group taken as a whole. Compare the ideal stoichiometric relationship corrected for deviation from ideality:

$$60\ CO+29.99\ O_2 \rightarrow 59.71\ CO_2+30.28\ TC;$$

with the average measurements for all five series corrected for errors of solubility,

$$60\ CO+30.03\ O_2 \rightarrow 59.72\ CO_2+30.28\ TC$$

The deviation is only

$$0.04\ O_2 \rightarrow 0.01\ CO_2+0.00\ TC.$$

These values represent milliliters. If the individual analyses were just that good, the analyst would be saved much effort.

Expressed in the ordinary fashion, the observed average values corrected for known solubility and deviation from ideality give the stoichiometric equation

$$2\ CO+1.001_0\ O_2 \rightarrow 2.000_0\ CO_2+1.000_3\ TC$$

If we assume that 0.04 ml of CO was generated during the absorption of excess oxygen in series 2 and 4, as previously indicated, the above equation may be corrected, and will then give the relationship

$$2\ CO+1.000_1\ O_2 \rightarrow 2.000_0\ CO+1.000_3\ TC.$$

A second stoichiometric relationship can be set up for series 1 to 4, inclusive, and a third for series 5, by assuming that the deviation of CO_2 is proportional to its partial pressure. This is by no means necessarily true [10], but the computation can be made for the sake of general interest, since it is often resorted to in so-called exact gas analysis. The equation for series 1 to 4 becomes

$$(60)\ (0.9997)\ CO+30(0.9994)\ O_2 \rightarrow 60\ (0.9963)\ CO_2, \quad (4)$$

which reduces to

$$60\ CO+29.99\ O_2 \rightarrow 59.80\ CO_2+30.19\ TC; \quad (5)$$

and that for series 5 becomes

$$(60)\ (0.9997)\ CO+30\ (0.9994)\ O_2 \rightarrow 60\ (0.9984)\ CO_2, \quad (6)$$

which reduces to

$$60\ CO+29.99\ O_2 \rightarrow 59.92\ CO_2+30.08\ TC. \quad (7)$$

Equations 5 and 7 are out of line with the observed data corrected for solution of CO_2. This method of calculation cannot be recommended in the present instance.

X. COMPUTATION AS AN UNKNOWN

So far the data have been treated on the basis of the known composition of the sample analyzed. Had this gas been submitted to the analyst as an unknown—and this represents the usual case—the data would have been computed on the assumption that other combustibles were present. It will be interesting to see what the resulting report would have been.

The data for the first series will be selected, since this more nearly represents average laboratory practice. Computed as though H_2 and CH_4 may have been present, according to the equation

$$H_2=TC-O_2$$

$$CH_4=O_2-1/3\ (CO_2+TC)$$

$$CO=1/3\ (4\ CO_2+TC-3\ O_2),$$

the analysis would have been reported:

CO, 99.3 percent

H_2, 0.6 percent

CH_4, 0.03 percent

Had the data been corrected for solubility of CO_2 in water and rubber, the analysis would have been reported

CO, 99.5 percent

H_2, negative

CH_4, 0.04 percent

Thus a sample of reasonably pure carbon monoxide would never be certified as such by the customary volumetric analysis.

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[10] This subject has been discussed previously [5, 7].

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DETERMINATION OF FREEZING POINTS AND AMOUNTS OF IMPURITY IN HYDROCARBONS FROM FREEZING AND MELTING CURVES[1] *

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ABSTRACT

Simple time-temperature freezing and melting curves are analyzed, and a procedure is outlined for determining from them the freezing point of a given substance and the amount of impurity in it. The procedure was applied to a number of different known solutions of hydrocarbons ranging from 0.006 to 0.115 mole fraction in concentration of solute. For the systems examined, it was found that the values for the freezing point of a given substance obtained from both freezing and melting curves were always in accord within their respective limits of uncertainty, and that the estimated amount of impurity was in error by not more than about 10 percent of itself, on the average.

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I. INTRODUCTION

In the work of the American Petroleum Institute Research Project 6 at this Bureau on the isolation and identification of hydrocarbons from petroleum, the freezing point of the "best" lot of each hydrocarbon has usually been determined by means of time-temperature freezing or melting curves, and the purity of it has usually been estimated from time-temperature freezing curves according to the method proposed by W. P. White [1].[3] In order to check the reliability of such measurements and their interpretation, the authors

[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received.

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[3] Figures in brackets indicate the literature references at the end of this paper.

have examined critically the principles and assumptions involved, and have made experimental observations on several hydrocarbon preparations (solutions) containing different known amounts of impurity (solute).

There are presented herewith the results of this study on the interpretation of time-temperature freezing and melting curves, together with a procedure for obtaining the proper value for the freezing point of a given substance (solution) and a reasonably reliable estimate of the amount of liquid-soluble, solid-insoluble impurity (solute) in it. From these values may be estimated the freezing point of the given substance when it contains no impurity. The apparatus and procedure are relatively simple and may be readily adjusted for observations on compounds having greatly different freezing points. With respect to the impurity in compounds of low impurity, the sensitivity is about 0.0001 mole fraction.

The authors wish to emphasize the fact that methods are available for determining, more accurately than is possible with the simple apparatus and procedure described in this paper, the freezing point of a substance, or the amount of impurity in it, or both. With a calorimetric assembly of the type used in the accurate measurement of heats of fusion and transition, and heat capacities of both the liquid and solid states, observations may be made of the temperature of equilibrium corresponding to various fractions of the substance melted. From these observations may be determined the freezing point and the amount of impurity, the latter with a sensitivity as great as 0.00001 mole fraction (see, for example, [2, 3]). With the same apparatus, measurements may be made of the apparent heat capacity of the "solid" at a number of temperatures below the freezing point, which will measure the amount of "premelting" at these temperatures. From these observations the amount of impurity may be calculated, with a sensitivity as great as 0.00001 mole fraction (see, for example, references [4, 5]).

A new method for determining the amount of impurity in a given "pure" substance is that recently developed at this Bureau by Schwab and Wichers [6]. This is a differential time-temperature freezing method involving observations on the given substance followed by duplicate observations on the same material plus a known amount of impurity. This differential method minimizes the experimental sources of error inherent in the simple method of making time-temperature observations only on the given substance, is well suited to the precise determination of small amounts of impurity, and has been satisfactorily tested on preparations of benzoic acid having amounts of impurity as low as 0.00001 mole fraction. However, the differential method cannot be used in those cases where it is necessary to retain the material under investigation in its original state of purity. This is important for hydrocarbons of high purity, which are usually available only in very limited quantities.

II. THEORETICAL PART

1. THERMODYNAMIC RELATION INVOLVED

For the equilibrium between a liquid phase consisting of two or more components and a crystalline phase consisting of one of those components, the thermodynamic relation between the temperature of

equilibrium and the composition of the liquid phase, in terms of that component (hereafter, for convenience, called the major component or solvent) present in the two phases, is [7, 8]

$$-ln\ N_1 = -ln\ (1-N_2) = N_2(1+1/2N_2+1/3N_2^2+\ \ldots) =$$
$$(\Delta H_{f0}/RT^2_{f0})\ \Delta T[1+(1/T_{f0}-1/2\Delta C_p/\Delta H_{f0})\Delta T+\ldots], \quad (1)$$

where N_1 is the mole fraction of the major component in the liquid phase, N_2 is $1-N_1$ or the sum of the mole fractions of all the other components in the liquid phase; R is the gas constant; T_{f0} is the absolute temperature of the freezing point of the given substance when pure (that is, when $N_1=1$ or $N_2=0$); ΔH_{f0} is the heat of fusion of the major component in the pure state at the temperature, T_{f0}; ΔC_p is, for the major component, the heat capacity of the liquid less that of the solid; and ΔT is $T_{f0}-T$, where T is the given temperature of equilibrium. In the derivation of eq 1, the assumptions involved are the following: (1) the liquid solution is ideal, or sufficiently dilute that the fugacity of the solute is proportional to its mole fraction; (2) the heat of dilution is negligible over the range of concentration from $N_1=1$ to the given value of N_1; and (3) the value of ΔC_p is constant over the range of temperature T to T_{f0}. When the values of ΔH_{f0}, T_{f0}, and ΔC_p are known, eq 1 permits evaluation of the mole fraction of liquid-soluble, solid-insoluble solute, N_2, from the value of the lowering of the freezing point, ΔT, and conversely evaluation of ΔT from the value of N_2.

For the substances with which the authors are primarily concerned, namely, the paraffin, naphthene (cycloparaffin), and aromatic hydrocarbons occurring in the gasoline and kerosene fractions of petroleum, the value of the term

$$1/T_{f0}-1/2\Delta C_p/\Delta H_{f0}$$

in eq 1 is small, and for several typical hydrocarbons of these classes, has the following values:

Compound:	$(1/T_{f0}-1/2\Delta C_p/H\Delta_{f0})$ deg^{-1}
n-Heptane	0. 0035
2,2,4-Trimethylpentane	. 0044
Methylcyclohexane	. 004
Benzene	. 003
Diphenylmethane	. 003
n-Dodecane	. 0030

The order of magnitude of this term for such hydrocarbons is seen to be 0.004/deg. Therefore, omission of the bracketed term on the right side of eq 1 will result in an error in the evaluation of N_2 from values of ΔT (or of ΔT from values of N_2) equal to (100)(0.004)(ΔT) percent of the value of N_2 (or of ΔT). That is to say, when ΔT has the values 0.1°, 1°, and 5°, the errors caused by the omission of the bracketed term will be of the order of 0.04, 0.4 and 2 percent, respectively, of the value of N_2 or of ΔT. Omission from eq 1 of the third and higher terms of the power series ($1/3\ N_2^2+\ \ldots$) on the left side will, for values of N_2 equal to 0.01, 0.05, 0.10, and 0.25 mole fraction, result in errors of 0.003, 0.08, 0.3, and 2 percent, respectively, of the value of N_2 or of ΔT.

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It appears, therefore, that in calculating values of N_2 from values of ΔT, or values of ΔT from values of N_2, when the amount of solute is less than one-fourth mole fraction and the value of ΔT is less than about 5° C, there may be used the simplified relation [4]

$$N_2(1+1/2N_2)=(\Delta H_{f0}/RT^2_{f0})\Delta T=A\Delta T, \tag{2}$$

without introducing from this source errors greater than about 2 percent of the value of N_2 or of ΔT, as the case may be.

2. DETERMINATION OF THE FREEZING POINT

In this paper, the freezing point of a given substance (solution) is taken to be that temperature at which crystals of the major component are in thermodynamic equilibrium with a liquid phase having the original composition of the given substance (solution). When, as is usually the case, the crystals of the major component are obtained from the solution itself, the freezing point is the temperature at which an infinitesimal amount of the crystalline phase of the major component is in thermodynamic equilibrium with the remainder of the substance in the liquid phase. The melting point of a given substance is thermodynamically identical with the freezing point as just defined.

No difficulty is normally experienced in determining, from time-temperature freezing curves, the value of the freezing point for a pure substance or for solutions (or impure substances) in which very little undercooling occurs. For substances containing significant amounts of impurity, or for solutions such as those used in determining molecular weights from the lowering of the freezing point, the occurrence of undercooling may produce significant errors if the freezing point is determined in the customary manner, even when thermodynamic equilibrium is established in the period immediately following the recovery from undercooling.

For such impure substances and solutions, undercooling produces a curve similar to that defined by the points *ABCDEF* in figure 1. In the interpretation of such a curve, two methods have been used to ascertain the freezing point. One method has been that of taking the freezing point to be the highest temperature actually observed after the onset of crystallization. This would be the temperature, T_K, corresponding to point K on the curve. Such a temperature is not characteristic of the given substance and has little thermodynamic significance other than that it is the temperature of equilibrium between the crystals of the major component and a liquid phase containing a greater concentration of impurity or solute than the original substance contained, and that the freezing point of the substance or solution is higher than this temperature. The other and much more usual method is to extrapolate the portion *EF* of the freezing curve back to its intersection at B'' with the line *ABC*. In a rigorous sense, this method also does not yield the proper value for the freezing point, and it will be shown in what follows that the freezing point is $T_{B'}$ $(=T_B)$, a temperature slightly below $T_{B''}$.

In figure 1, the curve *ABCDEF* represents a real freezing curve with undercooling, and the curve $A'B'EF$ represents an ideal curve

[4] For convenience, the cryoscopic constant, $\Delta H_{f0}/RT^2_{f0}$, is hereafter designated by the symbol A. The most simplified form of eq 1 is of course

$$N_2=A\Delta T.$$

with no undercooling. In the latter case, $T_{B'}$ (or T_B) is the true freezing point of the substance. When undercooling occurs, the substance and its container are for a time subjected to a smaller refrigerating head of temperature than would exist with no undercooling. The time required for a given amount of heat energy to be removed from the system during this period is therefore greater with undercooling than with no undercooling. If the ideal and real curves

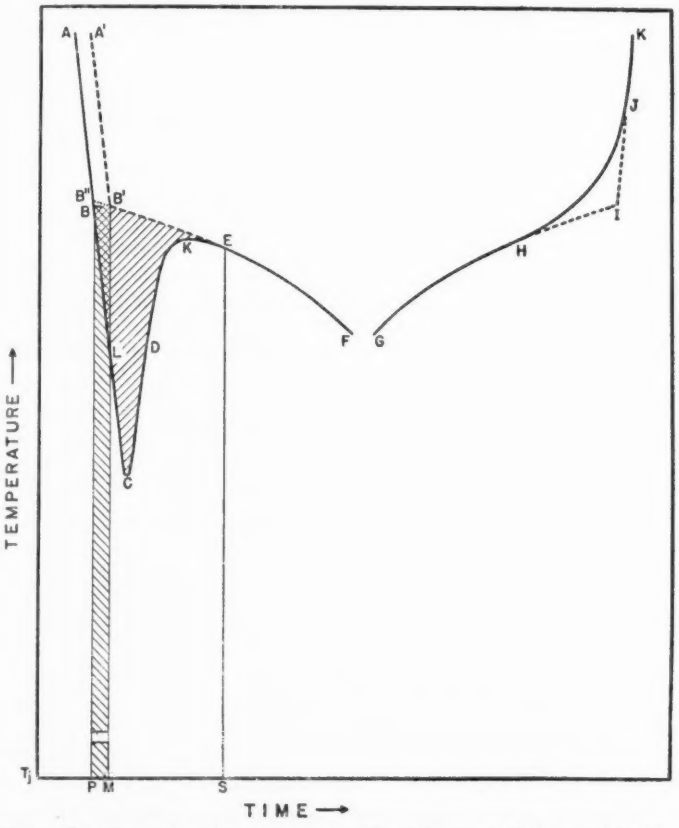

FIGURE 1.—*Diagram of a time-temperature freezing curve with considerable undercooling, and of a melting curve, both for the same impure substance.*

The scale of ordinates represents the temperature and the scale of abscissae the time. The diagram illustrates the method of determining the proper value of the freezing point and the initial time of freezing when undercooling occurs. See the text on p. 594–7 for explanation.

are made to coincide at E, then it follows that the time $z_E - z_B$ is greater than the time [5] $z_E - z_{B'}$.

On the real curve $ABCDEF$ in figure 1, point E represents the highest temperature at which thermodynamic equilibrium was established between the liquid and crystalline phases. With thermodynamic equilibrium existing in the given substance, the heat content of the substance and its container will be invariant at the temperature T_E,

[5] When a constant head of temperature is used, instead of a constant jacket temperature as in the present discussion, it is apparent that $z_E - z_B$ is equal to $z_E - z_{B'}$ and that $T_{B'}$ and $T_{B''}$ coincide.

and, likewise at the temperature T_B $(=T_{B'})$. Therefore, the decrease in heat content of the system as its temperature changes from T_B to T_E will be constant and independent of the path. So, for example, the decrease in heat content of the system as it passes from T_B to T_E along the path $BCDE$ will be the same as along the path $B'E$. That is to say,

$$H_B - H_E = H_{B'} - H_E, \tag{3}$$

where H is the heat content of the system in the given state. If T_j is the constant temperature of the fixed environment, T is the temperature of the substance and container, k is the coefficient of heat transfer, and z is the time, the quantity of heat passing from the substance and container to the jacket in any given time is, neglecting the energy of stirring, [6]

$$Q = k\int (T - T_j)dz. \tag{4}$$

Application of eq 3 and 4 to the curve in figure 1 gives

$$H_B - H_E = k(\text{area } BCDESP) = k(\text{area } BLMP) + k(\text{area } LCDESM), \tag{5}$$

$$H_{B'} - H_E = k(\text{area } B'ESM) = k(\text{area } B'LCDE) + k(\text{area } LCDESM). \tag{6}$$

Hence

$$\text{area } BLMP = \text{area } B'LCDE. \tag{7}$$

Adding the area BLB' to both sides of eq 7, there is obtained

$$\text{area } BB'MP = \text{area } BLCDEB'. \tag{8}$$

The relation given by eq 8 serves to locate the proper value of the freezing point $T_{B'}$ $(=T_B)$ on the line EF extended, such that the area $BB'MP$ is equal to the area $BLCDEB'$. These areas are shown cross-hatched in figure 1.

The figures summarized in table 1 serve to indicate under what conditions the value of $T_{B''} - T_{B'}$ is important and under what conditions it may be considered negligible. The values of $T_{B''} - T_{B'}$ given in table 1 were calculated on the basis that, with a given mass and heat capacity of substance and container, with a given heat of fusion of the substance, and with a given thermal insulation between the container of the substance and the jacket, the following conditions hold: (a) the cooling rate is 0.02°/min deg; (b) the total time of freezing of the pure substance is 40 minutes when the head of temperature is 50° C; (c) 0.01 mole fraction of solute produces a lowering of 0.3° C in the freezing point.

[6] To approach conditions of thermodynamic equilibrium it will be seen from section III–2 that stirring is required. In this case if u is the heat evolved in unit time by stirring, the equations corresponding to 4 and 7 are, respectively,

$$Q = k\int (T - T_j)dz + u\int dz$$

and $k(\text{area } BLMP) + u(z_{B'} - z_B) = k(\text{area } B'LCDE)$.

With an apparatus of the kind described in section III, the stirring energy is usually only several percent of the heat energy transferred as a result of the thermal head and consequently the term $u(z_{B'} - z_B)$ may be neglected in comparison with $k(\text{area } BLMP)$.

TABLE 1.—*Values of $T_{B''}-T_{B'}$ calculated for various conditions* [a]

Case	Time of freezing [a]	Head of temperature	Extent of undercooling	Concentration of solute [a]	$(T_{f_0}-T_f)$ [d]	Value of $T_{B''}-T_{B'}$	
						I [b]	II [c]
	min	*°C*	*°C*	*mole fraction*	*°C*	*°C*	*°C*
1a	40	50	5	0.002	0.06	0.0010	0.0014
1b	40	50	5	.02	.6	.010	.014
1c	40	50	5	.10	3.0	.045	.065
2a	40	50	1	.02	0.6	.0006	.0017
2b	40	50	5	.02	.6	.010	.014
2c	40	50	10	.02	.6	.036	.043
3a	200	10	5	.02	.6	.060	.066
3b	40	50	5	.02	.6	.010	.014
3c	20	100	5	.02	.6	.006	.010
4	200	10	5	.10	3.0	.27	.29

[a] See text for explanation.
[b] Calculated on the assumption of recovery from undercooling in 2 min.
[c] Calculated on the assumption of recovery from undercooling in 5 min.
[d] Lowering of the freezing point caused by the given concentration of solute.

From the values given in table 1, it is evident that, when the extent of undercooling is small in comparison with the head of temperature, the value of $T_{B''}-T_{B'}$ is small and of the order of several percent of $T_{f_0}-T_f$, the lowering of the freezing point caused by the given concentration of solute (or impurity). However, when the amount of undercooling is large in comparison with the head of temperature, as in case 4, the value of $T_{B''}-T_{B'}$ becomes quite important.

This method of determining the proper value of the freezing point is of importance in evaluating molecular weights by that cryoscopic method wherein the freezing points are determined from time-temperature curves. Frequently in such experiments, the thermal head is small and considerable undercooling occurs, and the foregoing correction is quite significant.

The freezing point as defined here is a definite temperature of equilibrium between the liquid phase and an infinitesimal amount of the crystalline phase of the major component. This equilibrium point can be approached from the low-temperature side as well as from the high-temperature side, that is, from a melting curve as well as from a freezing curve. On the right-hand side of figure 1, the curve *GHJK* is a melting curve in which the portion *GH* is assumed to represent thermodynamic equilibrium between the liquid and crystals of the major component. *HJ* is the portion during which the crystals and liquid still coexist but are no longer in thermodynamic equilibrium, and *JK* represents the warming curve for the liquid. The freezing point, T_I, as obtained by extrapolation of *GH* to its intersection with the extension of *KJ* at *I*, should be identical with the freezing point obtained by extrapolation of the freezing curve *FE* to $T_{B'}$, within the respective limits of uncertainty of the extrapolations, provided only that equilibrium does exist over the portions *GH* and *FE*. Except for ideally pure substances the curves *B'F* and *IG* are concave downward, and, if the rate of transfer of energy is the same in both cases (as assumed in figure 1), the curves will be mirror images of each other.

3. ESTIMATION OF THE AMOUNT OF IMPURITY

In the estimation, from time-temperature freezing curves, of the amount of solid-insoluble, liquid-soluble impurity in a given substance by any procedure based on the method of White [1], the following assumptions are made:

(a) The impurity remains entirely in the liquid phase, at least until the end of the period for which the lowering of temperature is determined.

(b) For a given head of temperature between the substance and the cooling jacket, the rate of crystallization of the substance is constant.

(c) At the times between which the lowering of the temperature is measured, the system of liquid and crystals is in thermodynamic equilibrium.

(d) The liquid-soluble, solid-insoluble impurity forms with the given substance in the liquid phase an ideal solution or a nonideal solution sufficiently dilute that eq 1 (or a simplified form of it) may be applied.

Let N_2^* be the mole fraction of impurity in the original substance, z_0 the time at which crystallization begins if no undercooling occurs (or, if undercooling occurs, the time at which crystallization would have begun in the absence of undercooling), z_f the time at which crystallization of the substance (major component plus impurity) is substantially complete (corrected, if necessary, for any significant change in the head of temperature and for any change in stirring), and r the fraction of the substance crystallized. Then, if the heat of fusion of the impurity is substantially the same as that of the major component,[7] the mole fraction of solute in the liquid phase at any time z, is

$$N_2 = N_2^*(z_f - z_0)/(z_f - z) = N_2^*/(1-r). \tag{9}$$

If the temperatures at the times z_0 and z are those of equilibrium between the liquid and crystalline phases and have the values T_{z_0} and T_z, respectively, then the lowering of temperature, $T_{z_0} - T_z$, is produced by an increase in mole fraction of solute in the liquid phase equal to

$$N_2 - N_2^* = N_2^*(z - z_0)/(z_f - z) = N_2^* r/(1-r). \tag{10}$$

For the investigations carried on in this laboratory (and probably in most others), the simplified eq 2 may, with appropriate limitations on the values of N_2 and $T_{f_0} - T_z$, be applied to determine the value of N_2^*. The following relation holds for the time z_0:

$$N_2^*(1 + 1/2N_2^*) = A(T_{f_0} - T_{z_0}). \tag{11}$$

Likewise, at the time z,

$$N_2(1 + 1/2N_2) = A(T_{f_0} - T_z). \tag{12}$$

Combination of eq 9, 11, and 12, with the elimination of T_{f_0} and N_2, yields the following relation for N_2^*, the wanted mole fraction of impurity in the original substance:

$$N_2^* = \frac{1-r}{2-r}\left(-1 + \sqrt{1 + \left(\frac{2-r}{r}\right) 2A(T_{z_0} - T_z)}\right) \tag{13}$$

[7] The effect of a difference in heat of fusion between the impurity and the major component is discussed in section III–4.

For values of r equal to 1/5, 1/4, and 1/3, the corresponding equations for N_2^* are as follows:

$$\text{For } r=1/5\text{: } N_2^*=\frac{4}{9}\left(-1+\sqrt{1+18A(T_{z_0}-T_z)}\right). \tag{14}$$

$$\text{For } r=1/4\text{: } N_2^*=\frac{3}{7}\left(-1+\sqrt{1+14A(T_{z_0}-T_z)}\right). \tag{15}$$

$$\text{For } r=1/3\text{: } N_2^*=\frac{2}{5}\left(-1+\sqrt{1+10A(T_{z_0}-T_z)}\right). \tag{16}$$

If, for any given case, the value of $1/2\ N_2$ is small enough in comparison with unity to be neglected, then combination of eq 9, 11, and 12 yields for N_2^* the simple relation

$$N_2^*=\frac{1-r}{r}A(T_{z_0}-T_z). \tag{17}$$

For values of r equal to 1/5, 1/4, and 1/3, the values of the coefficient $(1-r)/r$ are 4, 3, and 2, respectively.

When values of N_2^* and T_{z_0} are known, the value of T_{f_0}, the freezing point of the given substance when it contains no impurity, may be calculated from eq 11.

In order to evaluate N_2^*, it is necessary to determine the times z_0, z, and z_f and the temperatures T_{z_0} and T_z corresponding to z_0 and z. The three times must be corrected, if necessary, to a constant head of temperature, and, if necessary, for any significant change in the rate of introduction of energy by stirring; and the two temperatures must be determined from that portion of the freezing curve that corresponds to thermodynamic equilibrium between the liquid and crystalline phases.

The determination of the value of T_{z_0}, which is T_f, has already been discussed in the preceding part of this section.

The time z_0 is the time at which crystallization would have begun if no undercooling occurred, and, in figure 1, is the time at which the curve EF (representing equilibrium) extrapolates to the proper value, T_B', of the freezing point of the given substance.

There is next to be determined the proper final time of crystallization. The curve *ABCDEFGH* in figure 2 represents a time-temperature curve for a substance containing several mole percent of impurity made up of several components. In this example, the substance has all just crystallized at the temperature T_G. It will be noted that, contrary to the simple type of curve obtained with nearly pure substances, there is no sharp break to mark the time when all of the substance has crystallized. Since the head of temperature, and consequently the rate of transfer of heat, is continually decreasing, the cooling curve for the solid phase is concave upward, as from G to H, and approaches the temperature of the jacket asymptotically, the rate of change at any time being proportional to the head of temperature.

The curve *A'B'EFGH* represents the time-temperature curve for the same substance under similar conditions, but in the absence of undercooling. The curve *A'B'I'G'H'* represents a hypothetical process for the same system under similar conditions in which the crys-

tallization occurs at a constant head of temperature along the line $B'I'$, and then the solid phase is cooled along the line $I'G'H'$. There is required to be determined the time at I' at which all of the substance would have been crystallized had the head of temperature remained at the value $T_{B'}-T_j$ which it had at the beginning of crystallization at B'. In the actual process with no undercooling, as along the path $A'B'EFGH$, the substance has become all solid at the time G. Now

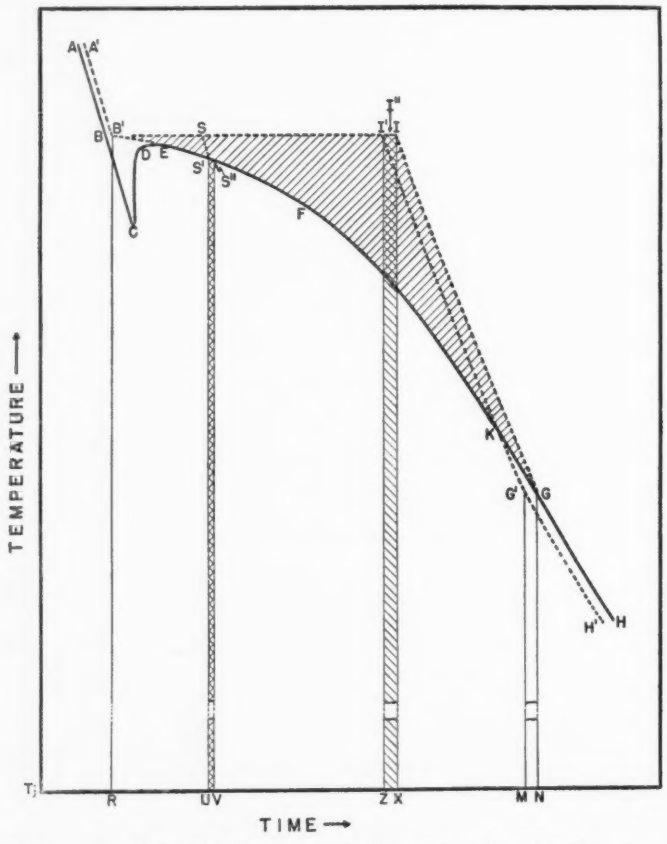

FIGURE 2.—*Schematic diagram of a time-temperature freezing curve.*

The scale of ordinates represents the temperature and the scale of abscissae the time. The diagram, which illustrates steps in the determination of the final time of freezing and of the equilibrium temperature at a selected time, is explained in the text on p. 599–601.

the time from B' to G is longer than the required time from B' to I' by the following two amounts: (a) the time from I' to G', which is the time required to cool the solid phase from the temperature $T_{I'}$ to the temperature $T_{G'}$; and (b) the time from I' to I, which accounts for the lower average head of temperature existing along the path $A'B'EFGH$ as compared with the path $A'B'I'G'H'$.

The point I' is located as follows: The curved line GH is extrapolated back to its intersection with a horizontal line through B' to locate the point I. This extrapolation can be made from the time-

temperature plot only if the distance from G to I is small, as in the case of a nearly pure substance with a large head of temperature, when the line will appear substantially straight. In most cases, however, it is necessary to plot the logarithm of the head of temperature against the time, as in figure 3, in which case the line GH is linear and can be readily extrapolated back to locate the point I. The points G and I are then located in figure 2 from their values of time and temperature as determined in figure 3. The point I' is then located on the line $B'I$ by making the area $KGNMG'$ equal to the area $B'I'KFE$ or, what is equivalent and simpler, the area $I'IXZ$ equal to the area $B'IGFE$. The lines $I'G'H'$ and IGH are parallel and represent the same process in the same length of time but occurring at different times. That this is the proper location of the point I', may be proved by the same argument as on page 596. Since $T_{G'}$

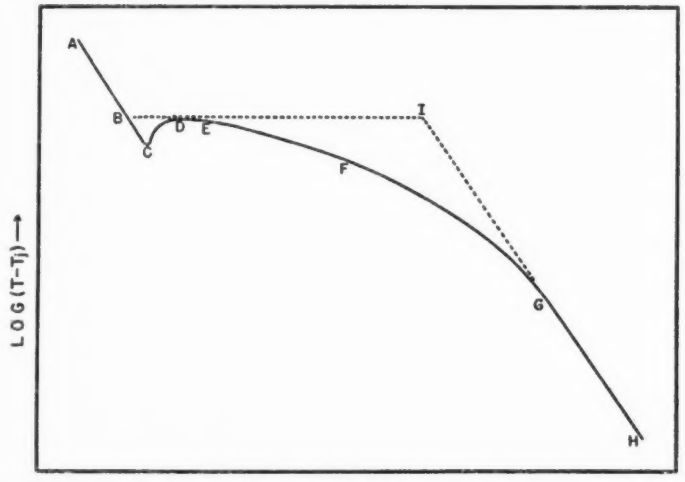

FIGURE 3.—*Diagram showing the method of plotting a freezing curve to determine the total time of freezing.*

The scale of ordinates represents the logarithm of the head of temperature, log $(T-T_f)$, and the scale of abscissae represents the time. See the text on p. 601 for explanation.

and T_G are equal and the system is the same in the two cases, then the change in heat content along the path $B'EFG$ is the same as along the path $B'I'G'$. Therefore,

$$k(\text{area } B'I'G'MR)=k(\text{area } B'EFGNR) \tag{18}$$

and hence

$$\text{area } B'EFKI'=\text{area } KGNMG'. \tag{19}$$

It can also be shown, by proceeding along the path $B'EFG$ and then along the path $B'I'ZXIG$, that

$$\text{area } I'IXZ=\text{area } B'IGFE. \tag{20}$$

In actual practice, the point I' is located directly by making the area $I'IXZ$ equal to the area $B'IGFE$. The time at I' is taken as the value of $z_{f'}$. In determining $z_{f'}$, the following points may be noted: (a) When the head of temperature is large, $(T_{B'}-T_j)$, or IX, will be large,

and to balance a given area $B'IGFE$, $I'I$ may be small; (b) when the substance is relatively pure (containing about 0.01 mole fraction or less of solute), the area $B'IGFE$ will be small, and the points I' and I will be nearly identical.

In the case of relatively pure substances and with a large head of temperature, a time-temperature curve will be obtained in which a simple extrapolation of the final slope to its intersection at the value of T_{z0} will suffice to determine the value of $z_{f'}$ within the significance of the present investigation.

The value of $z_{f'}$ determined in the manner just outlined is subject to one further correction, resulting from the fact that the energy of stirring was not contributed to the system during all the time $z_{f'}-z_0$, but only during the first part of that time (see section III–3). This correction is made as follows:

Let z_{ss} be the time at which the stirrer is stopped. Then the correction to $z_{f'}$ is simply the number of minutes that would have been required for the energy of stirring, over the time $z_{f'}-z_{ss}$, to be transferred to the jacket at the rate at which it was transferred during the first part of the freezing experiment. If u is the energy of stirring, per unit of time, ΔH (fusion) is the molal heat of fusion of the substance and m and M are its mass and molecular weight, respectively, then the rate at which energy is transferred to the jacket during crystallization at the initial head of temperature may be taken approximately as $(m/M)\Delta H_f/(z_{f'}-z_0)$. The additional energy that would have had to be transferred to the jacket had the stirring continued over the period z_{ss} to $z_{f'}$ may be taken as $u(z_{f'}-z_{ss})$, and the additional time required for the transfer of this amount of energy is

$$\Delta z_f=\frac{u(z_{f'}-z_{ss})\ (z_{f'}-z_0)}{(m/M)\Delta H_f}. \tag{21}$$

For example, if u is 0.02 j/sec or 0.3 cal/min, m/M is 1/3 mole, ΔH_f is 2,400 cal/mole, $z_{f'}-z_0$ is 100 min, and $z_{f'}-z_{ss}$ is 80 minutes, then the time to be added is 3 min, which is a correction of 3 percent. In general, this correction to the time of crystallization, because of the lack of stirring in the latter part of the experiment, will be significant when the time over which the stirrer is not in operation is large, when the stirring energy per unit of time is large, and when the total heat of fusion of the substance is small. The accuracy of this correction will depend largely upon the constancy of the energy of stirring, which will be discussed in section III–4.

In figure 2 on the line $B'I'$ extended, there is located the point I'' so that the time from I' to I'' is equal to Δz_f or $z_{f'}-z_f$, as given by eq 21. This point I'' corresponds to the final time corrected to the head of temperature $T_{z_0}-T_j$ and corrected for stirring. There now remains to be determined T_z, the temperature at the time z. The time z should be taken as large as possible without going beyond the time at which equilibrium exists between the liquid and crystalline phases (see point F in fig. 5). Referring to figure 2, there is first located the point S on the line $B'I''$ so that $B'S$ is a known fraction of $B'I''$. From S a line is drawn parallel to AB, intersecting EF at S'. The value of T_z corresponding to the selected time z is that at a point S'' located on the curve EF at a point slightly below S' so that the area $B'SS'$ is equal to the area $S''S'UV$. Except in the case of very impure sub-

stances, or, in those cases where the head of temperature is relatively small, the area $B'SS'$ will be small and S'' will not differ significantly from S'. The effect of stirring on the relation between S' and S'' is the same as that discussed in section II–2 on the relation between B and B' in figure 1.

It should be noted that in the foregoing procedure there is little uncertainty in determining the values of z_0 and T_{z_0}. Likewise, there is little uncertainty in determining the value of T_z corresponding to a given z, once the value of z_f is fixed. Therefore, practically all of the uncertainty in the estimation of the amount of impurity by this method lies in the determination of the proper value of z_f, defined as the time at which the substance would have been substantially all crystallized had the rate of crystallization remained constant; that is, at its value at the beginning of the freezing period.

In addition to those factors whose effect upon the rate (and hence the total time) of crystallization have been evaluated quantitatively, there exist other factors which are not amenable to such evaluation and which may contribute important uncertainties in the determination of the total time, $z_f - z_0$, as just outlined. Since all except one of these factors may be varied in magnitude by appropriate change in the experimental apparatus and procedure, they are discussed in section III–4.

In case the substance is one for which the heat of fusion is not known, an estimate of it may be made by a comparison with observations on a substance whose heat of fusion is known. The procedure is as follows (see also [18]): Select a similar substance A, whose heat of fusion is known and whose freezing point is within about 20° C of that of the substance B, whose heat of fusion is to be estimated. Let m_A, M_A, and $(\Delta H_f)_A$ be the mass, molecular weight, and heat of fusion of the substance A, and, likewise, m_B, M_B, and $(\Delta H_f)_B$ those for the substance B. Perform a complete time-temperature freezing experiment on the substance A, and likewise on the substance B, using the same volume of substance in each case and the same jacket temperature, T_j. From the time-temperature curve for A, determine $(z_f - z_0)_A$, the corrected total time of freezing, and likewise $(z_f - z_0)_B$ from the curve for B. From these two experiments, the heat of fusion of the unknown substance B may be calculated in two different ways.

One method utilizes the value of the head of temperature for each experiment together with the assumption that the coefficient of heat transfer, k, is the same in the two experiments. Then

$$(m/M)_A(\Delta H_f)_A = k(z_f - z_0)_A(T_{z_0} - T_j)_A, \tag{22}$$

and

$$(m/M)_B(\Delta H_f)_B = k(z_f - z_0)_B(T_{z_0} - T_j)_B. \tag{23}$$

On eliminating k there is obtained

$$(\Delta H_f)_B = (\Delta H_f)_A \frac{(m/M)_A\ (z_f - z_0)_B\ (T_{z_0} - T_j)_B}{(m/M)_B\ (z_f - z_0)_A\ (T_{z_0} - T_j)_A}. \tag{24}$$

The heat transfer coefficient will be constant within the required limits if the evacuated space of the freezing tube has been sealed off, the jacket temperature is made the same for both A and B, and the two experiments are performed at not greatly different times.

The other method utilizes for each experiment the value of the effective heat capacity of the system, including C, that of the hydrocarbon, and c, that of the thermometer, stirrer, and container, together with the value of $(dT/dz)^*$, the rate of change of temperature with time at the temperature T_{z_0} just before crystallization begins. The value of $(dT/dz)^*$ is determined from the freezing curve obtained on the "unknown," B. The value of c, the effective heat capacity of the container, etc., is determined from complete time-temperature freezing curves obtained for substances having known heats of fusion and known heat capacities in the liquid state near the freezing point, and having freezing points higher and lower than those of the "unknowns" to be investigated. The relation employed to evaluate c at the desired temperatures is

$$c=\frac{(m/M)_A(\Delta H_f)_A}{(z_f-z_0)_A(dT/dz)^*_A}-C_A. \tag{25}$$

The heat of fusion of the "unknown" B is given by the relation

$$(\Delta H_f)_B=\frac{(c+C_B)\ (dT/dz)^*_B(z_f-z_0)_B}{(m/M)_B}. \tag{26}$$

The heat capacity of the hydrocarbon B in the liquid state at the given temperature may, if not known, be assumed equal to the heat capacity of that mass of a hydrocarbon of similar size and type having the same volume at room temperature. In an apparatus of the kind described in section III–1, the hydrocarbon (50 ml at room temperature) contributes about 80 percent of the effective heat capacity of the system. Examination of the available data indicates that for the hydrocarbons, *n*-hexane, *n*-heptane, 2-methylhexane, 2,2,4-trimethylpentane, methylcyclopentane, cyclohexene, methylcyclohexane, 1,2-dimethylcyclopentane, and 1,2,4-trimethylbenzene, those masses of hydrocarbon which are contained in a volume of 50 ml at 20° C will have, in the liquid state, heat capacities ranging as follows: at 0° C, 15.8 to 18.0 cal/deg; at −50° C, 14.3 to 16.7 cal/deg; at −75° C, 13.9 to 16.5 cal/deg. The variation between compounds of the same size and type is smaller than this.

If the heat of fusion is known for the substance, B, whose amount of impurity is to be determined, and if the coefficient of heat transfer is known for the given jacket conditions, the amount of impurity may be calculated entirely from the first part of the freezing curve for the substance B. The rate at which heat is being removed from the substance during crystallization at the temperature T is $k\ (T-T_f)$, and, therefore, the time during which any given fraction, r, of the substance will have crystallized is

$$z-z_0=\frac{r(m/M)_B(\Delta H_f)_B}{k(T-T_f)_B}. \tag{27}$$

The lowering of the equilibrium temperature from the time z_0 to the time z gives the value of $T_{z_0}-T_z$ corresponding to the given value of r, from which the amount of impurity may be calculated using eq 13 or 17.

Likewise, if the heat of fusion is known for the substance whose amount of impurity is to be determined, and if the effective heat capacity of the container, etc., is known for the given temperature, the amount of impurity may be calculated entirely from the first part of the freezing curve for the given substance. In this case, the rate at which heat is being removed from the substance during crystallization at T_{z_0} is $(c+C_B)\ (dT/dz)^{\cdot}_B$, and, therefore, the time during which any given fraction, r, of the substance will have crystallized is

$$z-z_0=\frac{r(m/M)_B(\Delta H_f)_B}{(c+C_B)\ (dT/dz)^{\cdot}_B}. \tag{28}$$

As before, the lowering of the equilibrium temperature from the time z_0 to the time z gives the value of $T_{z_0}-T_z$ corresponding to the given value of r, from which the amount of impurity may be calculated using eq 13 or 17.

The foregoing methods of estimating the amount of impurity from a partial time-temperature curve [8] may be particularly useful in the case of substances (such as the methylcyclohexane described in connection with fig. 8) for which no part of the freezing curve represents thermodynamic equilibrium between liquid and solid. In such cases, the melting curve may be utilized, operating just as with a freezing curve except the reverse in point of time. The value of k must be evaluated for the given jacket conditions, and the value of $(dT/dz)^*$ must be evaluated for the head of temperature corresponding to $T_j-T_{z_0}$.

III. EXPERIMENTAL PART

1. APPARATUS

A simple form of apparatus for obtaining time-temperature freezing and melting curves of the kind discussed in this report is shown in figure 4. This is substantially the same apparatus previously described by one of the authors (B. J. M. [9]). In figure 4, A is the evacuated double-walled flask containing the substance under investigation; B is a larger Dewar flask containing the liquid providing the constant temperature cooling or warming jacket; C is the platinum resistance thermometer (Leeds & Northrup No. 8163); D is the stirrer, made of No. 15 AWG Nichrome wire and operated with a reciprocating stroke 5 cm long at a frequency of 85 to 120 strokes per minute; E is a cork stopper. Tube A has an inside diameter of 2.5 cm and a length of 29 cm, and is normally filled to a depth of about 11 cm. F is a thin, metal protecting tube.

With a stirrer which fits the containing tube closely, the accumulation of solid on the walls soon causes labored stirring. For this reason, a clearance of 1 to 2 mm is provided between the stirrer, D, and the inner walls of tube A. In the case of most hydrocarbons, it is possible to stir the substance until the time at which it is from one-fourth to one-third crystallized, with the longer times usually occurring with the more impure samples.

[8] The authors acknowledge the benefits of discussion of these points with C. S. Cragoe of this Bureau.

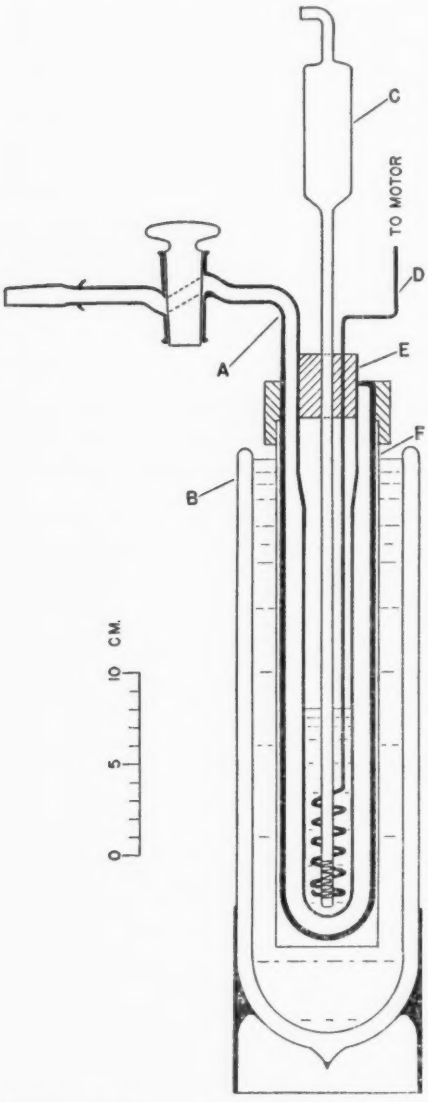

FIGURE 4.—*Schematic diagram of the apparatus used in obtaining time-temperature freezing and melting curves.*

See the text on p. 605 for explanation.

For substances having freezing points below room temperature, the most readily available materials for controlling the temperature of the jacket are ice, solid carbon dioxide, and liquid air. After the refrigerant suitable for the experiment in question has been selected, the thermal conductivity is adjusted to the desired value, as previously described [9], by changing the degree of evacuation of the double-walled tube. This tube, which is silvered to reduce heat transfer by radiation, is connected to a high-vacuum oil pump through a ground-glass joint, in place of the usual rubber connection. In this way, a sufficiently low pressure is obtainable within a few minutes with a good pump.

The resistance of the platinum thermometer is measured on a Mueller resistance bridge (Leeds & Northrup No. 8067) with a sensitivity on the galvanometer scale of 1.7 mm per 0.001° C.

With 50 ml of the hydrocarbon in the apparatus at about −80° C, the effective heat capacity of the substance and container, including appropriate portions of the thermometer and stirrer, is about 90 j/deg, of which about 70 percent is due to the hydrocarbon.[9] With the same amount of the same hydrocarbon at −80° C, the energy of stirring at the rate of 85 strokes per minute was determined to be 0.020 ±0.006 j/sec.[10] Except for small rates

[9] The calculation was actually made for 2,2,4-trimethylpentane, but the result will be roughly the same for the same volume of any liquid hydrocarbon at this temperature [16].

[10] The energy of stirring was determined by having the substance and container at about the temperature of the jacket, taking observations of temperature, with stirring, for a period of 12 to 15 min, stopping the stirrer for a known time of 3 to 5 min, again taking observations of temperature, with stirring, for another period of 12 to 15 minutes, etc. The cessation of stirring in a given period produces, between the two periods adjacent to it, an offset (decrease) of the time-temperature curve with respect to the temperature. Multiplication of this lowering of temperature by the heat capacity of the system gives the energy of stirring for the given period.

of transfer of heat energy to the cooling jacket, stirring energy of this magnitude may be considered almost negligible. With 50 ml of the hydrocarbon, 2,2,4-trimethylpentane, in the apparatus at about −108° C and with a jacket temperature of −185° C and a consequent head of temperature of 77° C, the rate of transfer of heat energy to the jacket was calculated to be 1.2 ±0.2 j/sec, when the Dewar flask was evacuated to a point that gave a lowering of 0.8° C/min for this system at this head of temperature. In this example, the stirring energy is nearly 2 percent of the total energy being transferred, and may be significant in connection with the determination of the total time of freezing (see section II–3).

2. ATTAINMENT OF EQUILIBRIUM

In order for the measurement of the temperature in a system of liquid and crystals to have thermodynamic significance, it is important to know that the system is in the state of thermodynamic equilibrium corresponding to that temperature. In figure 5 are shown three time-temperature curves obtained on a solution of 2,2,4-trimethylpentane containing 0.0266 mole fraction of solute (methylcyclohexane), using liquid air (temperature about −185° C), in the cooling jacket for the freezing curves and solid carbon dioxide (temperature about −80° C) for the melting curve. The time-temperature freezing curve shown in the upper left of the figure was obtained with the stirrer in operation up to the time designated by *SS*, while the stirrer was in operation throughout the determination of the melting curve shown in the upper right of the figure. However, in obtaining the freezing curve shown in the lower left of the figure, stirring was stopped at the time (designated by *SS*) shortly before complete recovery from undercooling. It was pointed out in section II–2 that extrapolation of the freezing and melting curves should lead to identical values for the freezing point within their respective limits of uncertainty, provided that equilibrium exists over the portions of the curve used in the extrapolation. Since extrapolations of the portions *FE* and *KL* (obtained with stirring) of the upper freezing and melting curves do give substantially the same value for the freezing point (−108.015 and −108.010° C), it seems reasonable to conclude that over the portions *FE* and *KL* equilibrium was established (or a uniform departure from equilibrium occurred in both the freezing and melting experiments in such a way as to make them yield the same value for the freezing point on extrapolation). Extrapolation of the lower freezing curve, in which stirring was stopped before complete recovery from undercooling, yields the value −108.136° C, which is more than 0.1° C too low, and shows that equilibrium was not established over the portion of the curve used in this extrapolation.

Adequate stirring is necessary to establish and maintain equilibrium. This is also evident from the upper freezing curve, where there is a marked inflection at the point, *F*, at which time the stirrer stopped. In the period *FG*, during which the stirrer is no longer in operation, the temperature as recorded does not correspond to equilibrium for the given system of liquid and crystals. This change in slope at or preceding the cessation of stirring is characteristic of these curves and has been reported previously [9].

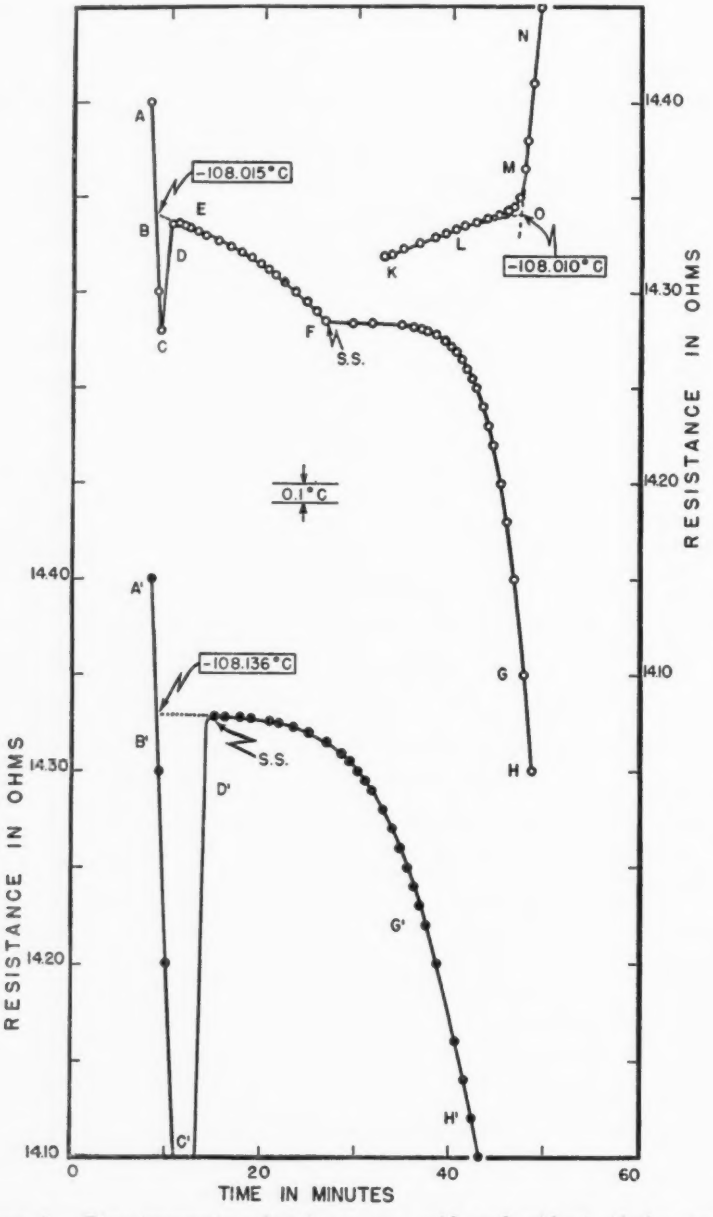

FIGURE 5.—*Time-temperature freezing curves, with and without stirring, and a melting curve, with stirring, all taken on the same solution.*

The scale of ordinates gives the resistance in ohms of the platinum-resistance thermometer (0.1 ohm ≈ 1° C) and the scale of abscissae gives the time in minutes. The solution consisted of 2,2,4-trimethylpentane with 0.0266 mole fraction of solute (methylcyclohexane). See the text on p. 607 for explanation.

Additional evidence that such a system is substantially in thermodynamic equilibrium over the portions of the curve indicated is provided in tables 3 and 4. In table 3, accord is shown between the experimentally determined freezing points and the values of the freezing points calculated from the known values of the mole fraction of solute, which indicates that at least the system was in substantial equilibrium near the freezing point. In table 4 is recorded the agreement between the known mole fraction of impurity and that evaluated from the lowering along the freezing curve. This establishes that the temperatures along the freezing curves, in the absence of compensating errors, were substantially equilibrium temperatures within the significance indicated.

There are some substances whose crystallization behavior is such that approach to thermodynamic equilibrium is not normally attained in the freezing experiment with stirring. A case of this kind is discussed on p. 612.

3. DETERMINATION OF THE FREEZING POINT

As mentioned previously, extrapolation of the equilibrium portions of the freezing and melting curves should lead to identical values for the freezing point of a substance within the respective limits of uncertainty of the extrapolation. It is advisable, therefore, to check the reliability of the freezing point both from the freezing and melting curves. In general, the reliability of the value depends upon the extent of the extrapolation involved, the reliability increasing markedly with decrease in the extent of the extrapolation. Usually, as may be seen from figures 6 and 7, which are self-explanatory, the freezing curve yields the more reliable value of the freezing point for the less concentrated solutions, whereas the melting curve yields the more reliable value for the more concentrated solutions. In any case, the two values of the freezing point determined from the freezing and melting curves should be in accord within the limits of uncertainty associated with the extrapolation of the respective curves, and a "best" value may be obtained by appropriate weighting of these two values.

As pointed out previously, in the case of substances having a significant amount of impurity, both the freezing and melting curves should be concave downward, and, if the rate of transfer of energy is the same in both cases, they should be mirror images of each other. If, then, a melting curve is obtained which has no portion concave downward, it is certain that equilibrium has not been attained. In such cases, the experiment should be repeated, with the system containing more of the crystalline phase before melting begins, or with a smaller rate of heat transfer, or preferably both, in order to obtain a sufficient portion of the melting curve in equilibrium (that is, concave downward) to permit reasonably reliable extrapolation of it to the liquid line. In the extrapolation of melting curves, one must guard against the tendency to consider as equilibrium measurements some of the points immediately following the point of inflection,[11] which separates the part of the curve that is concave downward (equilibrium) from the part concave upward (nonequilibrium), and consequently

[11] This point of inflection in the melting curve can be located easily by plotting with the time scale compressed much more than usual.

to obtain, on extrapolation of the melting curve, a value of the freezing point higher than the proper one. With these precautions, time-temperature freezing and melting curves obtained with the apparatus

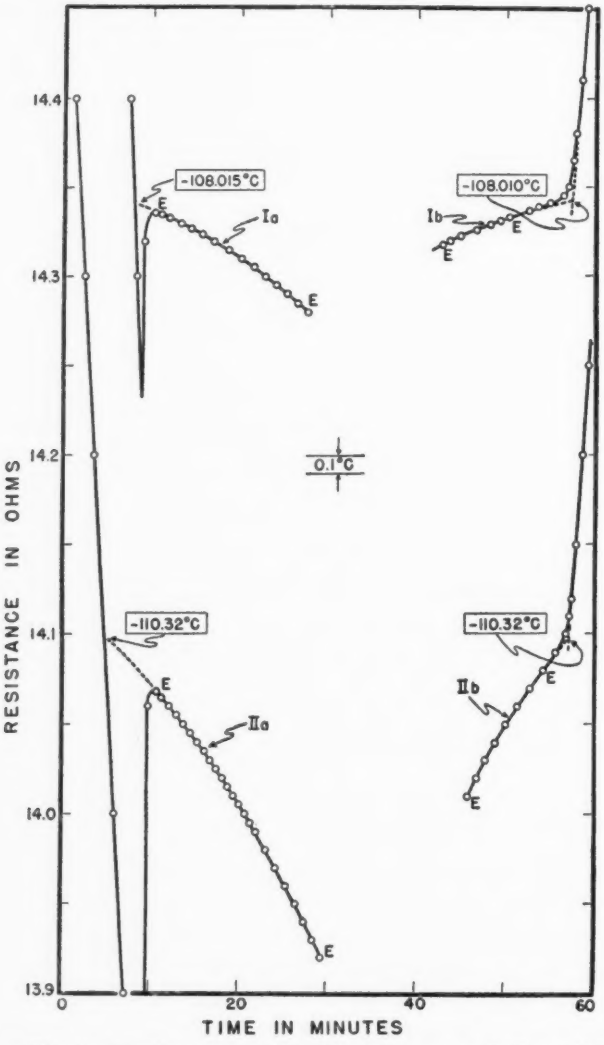

FIGURE 6.—*Time-temperature freezing and melting curves for two different concentrations of the same solution.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer (0.1 ohm ≈ 1° C), and the scale of abscissae gives the time in minutes. The upper curves were obtained on a solution of 2,2,4-trimethylpentane containing 0.0266 mole fraction of solute (methylcyclohexane) and the lower curves on the same system with the mole fraction of solute equal to 0.1147.

and procedure described in this paper, and with substances that crystallize normally, will yield values of the freezing point that are in accord within about 0.01° C or better. It should be emphasized that

the downward concavity is a necessary but not a sufficient criterion of equilibrium.

In table 2 are presented data showing the effect of heat transfer upon the reproducibility of the values of the freezing point obtained from freezing curves and of the values obtained from melting curves, and the effect upon the degree of accord of the values from the freezing curves with those from the melting curves. These data, taken with the apparatus described in this paper and with *n*-dodecane containing

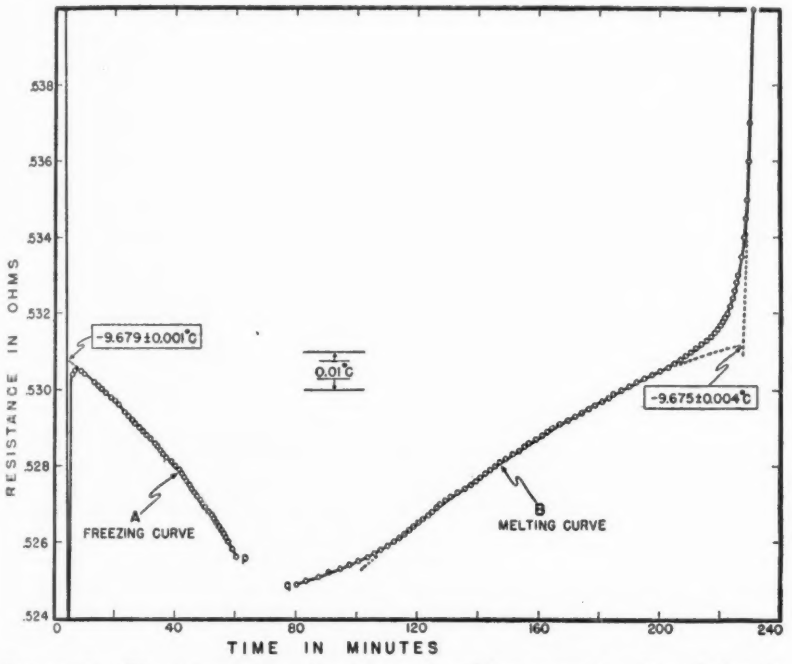

FIGURE 7.—*Time-temperature freezing and melting curves for determining the freezing point of a solution of n-dodecane containing 0.0062 mole fraction of solute (1,2,4-trimethylcyclohexane).*

The scale of ordinates gives the resistance of the platinum thermometer in ohms (0.1 ohm ≈ 1° C). The scale of abscissae gives the time in minutes. The circles about the observed points are drawn with radii equal to 0.0005° C. See the text on p. 609.

0.0012 mole fraction of impurity, show that (a) the value of the freezing point obtained from the freezing curves is substantially independent of the rate of heat transfer for the nearly fourfold increase from 0.4 to 1.5° C/min [12]; (b) the value of the freezing point obtained from the melting curves is significantly affected by the rate of heat transfer, the value obtained increasing with increase in the rate of heat transfer; (c) the most reliable value of the freezing point for this nearly pure substance is that obtained from the freezing curves.

[12] See footnote a in table 2.

TABLE 2.—*Data showing the effect of the rate of heat transfer on the value of the freezing point determined on a lot of n-dodecane containing 0.0012 mole fraction of impurity, as obtained both from freezing and melting curves*

Experiment	Freezing part		Melting part	
	Rate prior to crystallization [a]	Freezing point determined [b]	Rate after melting [a]	Freezing point determined [b]
	° C/min	° C	° C/min	° C
1	1.4	−9.590±0.001	0.1	−9.582±0.008
2	0.45	−9.589±0.001		
3	1.5	−9.589±0.001	.1	−9.584±0.005
4			.25	−9.581±0.008
5	0.4	−9.590±0.001	.004	−9.587±0.003

[a] The effective heat capacity of the system is about 100 j/deg (24 cal/deg). Therefore with a hydrocarbon in the liquid phase just before crystallization or just after melting, a rate of change of temperature of the system of 1° C/min corresponds to a rate of heat transfer of about 100 j/min.

[b] The uncertainty assigned includes only that involved in extrapolation of the equilibrium portion of the respective freezing and melting curves.

The freezing curves A and A' in figure 8 illustrate the case in which, even for a fairly pure compound (here, methylcyclohexane having an

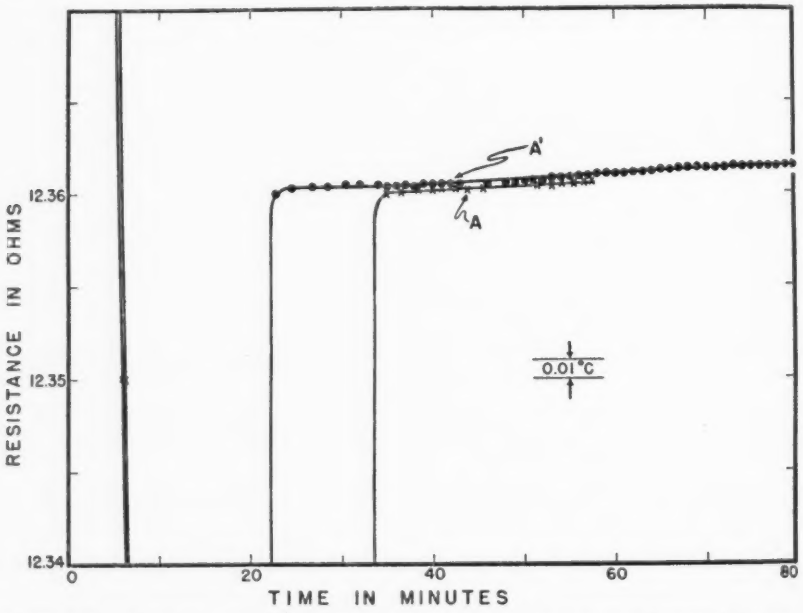

FIGURE 8.—*Time-temperature freezing curves illustrating a case of nonequilibrium.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer (0.1 ohm ≈ 1° C) and the scale of abscissae gives the time in minutes. The two freezing curves were obtained on a sample of methylcyclohexane containing about 0.005 mole fraction of impurity. See the text on p. 612-13 for explanation.

impurity of about 0.005 mole fraction), the extent of undercooling, or the abnormal crystallizing behavior, or both, is so great as to render invalid, as far as thermodynamic equilibrium is concerned, the part of the freezing curve that, with stirring, is normally the portion representing thermodynamic equilibrium. It will be noticed that no portion

of these curves is concave downward. Instead, even 70 min after the onset of crystallization, the temperature is still rising. The curve A' was obtained from an experiment repeating that from which curve A was obtained, with the hydrocarbon having been kept at a temperature always below −80° C during the intervening period of 1 day, and with seeding with a cold wire in order to induce crystallization during the freezing period and to reduce the extent of undercooling.[13] It will be noticed that the characteristics of this curve are no better than those of curve A. The only conclusion which can be drawn from such curves is that the freezing point is higher than the highest temperature observed after crystallization begins. In such cases, the proper value of the freezing point must be determined from time-temperature melting curves.

In table 3 are presented data showing the results of determinations of the values of the freezing point, obtained both from freezing and melting curves, for several hydrocarbon systems containing known amounts of solute. There are also included in the table values of the freezing point calculated for the corresponding ideal solutions by means of eq 1. The three substances used as the main components were lots of 2,2,4-trimethylpentane, *n*-dodecane, and toluene. These were found to contain impurities in the amount of 0.0018, 0.0012, and 0.0005 mole fraction, respectively, as determined by the method described in section II–3 of this paper. The freezing points for samples containing zero mole fraction of impurity were calculated by correcting the freezing points determined for these actual samples for the lowering caused by the given small amount of impurity, by means of eq 1. For the several solutions, the original amount of impurity in the main component was included with the amount of known solute added to obtain the total concentration of solute. It may be noted that the values of the freezing point determined from the freezing curves and from the melting curves are in excellent accord, where both were determined. Also, the accord of these values with those calculated for ideal solutions of the same concentration indicates that, over these ranges of concentration, such hydrocarbon systems are substantially ideal, or are ones in which the fugacity of the solute is proportional to its mole fraction. In these calculations, the following auxiliary data were used: for 2,2,4-trimethylpentane, $\Delta H_{f_0}=2201.6$ cal/mole and $\Delta C_p=7.1$ cal/mole, from Pitzer [14]; for *n*-dodecane, $\Delta H_{f_0}=8{,}743$ cal/mole and ΔC_p 13.45 cal/mole, from Huffman, Parks, and Barmore [11]; for toluene, $\Delta H_{f_0}=1{,}580$ cal/mole from Parks and Huffman [12], and $\Delta C_p=7$ cal/mole, estimated; $R=1.98714$ cal/deg mole and 0° C=273.16° K [13, 20].

[13] It has been observed by a number of investigators in this and other laboratories that (a) seeding with crystals and (b) maintaining the hydrocarbon for an appreciable time at a temperature just below its freezing point serve to facilitate the formation of crystals. See also [10].

TABLE 3.—*Values of the freezing points of known solutions of hydrocarbons, determined both from freezing and melting curves*

Solution			Freezing point of the solution		Freezing point of the ideal solution
Main component	Solute added	Concentration of total solute	From the freezing curve[a]	From the melting curve	
		Mole fraction	*°C*	*°C*	*°C*
2,2,4-Trimethylpentane		0.0000	(−107.347)		(−107.347)
Do		.0018	−107.394		
Do	*n*-Heptane	.0113	−107.640	−107.638	−107.629
Do	do	.0113	−107.643		−107.629
Do	Methylcyclohexane	.0266	−108.015	−108.010	−108.014
Do	do	.0266	−108.005		−108.014
Do	do	.0727	−109.18		−109.20
Do	do	.1147	−110.32	−110.32	−110.32
n-Dodecane		.0000	(−9.570)		(−9.570)
Do		.0012	−9.589	−9.587	
Do	1,2,4-trimethylcyclohexane.	.0062	−9.679	−9.676	−9.668
Do	do	.0062	−9.678		−9.668
Toluene		.0000	(−94.983)		(−94.983)
Do		.0005	−95.005		
Do	*m*-Xylene	.0126		−95.511	−95.492

[a] The values in parentheses for zero mole fraction of impurity were obtained by correcting, with the aid of eq 1, the freezing points of the actual samples for the lowering caused by the small amounts of impurity they contained.

4. ESTIMATION OF THE AMOUNT OF IMPURITY

In the experimental determination of the amount of impurity by the procedures outlined in section II–3 and with an apparatus similar to that described in section III–1, there exist a number of factors whose influence cannot be evaluated quantitatively and which may contribute significant uncertainties in the estimation of the amount of impurity. These factors include (a) change in volume of the substance on crystallization, (b) accumulation of solid substance on the walls of the container during crystallization, (c) nonuniformity of temperature throughout the substance after cessation of stirring, (d) change in the energy of stirring, (e) incomplete crystallization of the substance, (f) difference in heat of fusion between the impurity and the major component, and (g) inclusion of solute within the crystals of the major component. Of these factors, all but (f) are ones whose influence may be altered by appropriate change in the experimental arrangements.

The effect of the change in volume of the substance as it passes from the liquid to the solid state is to change the rate of heat transfer between the container and the jacket. For hydrocarbons, the change in volume from liquid to solid is negative, so that the rate of heat transfer will decrease as the crystallization proceeds. If that part of the wall of the container which is touched by the hydrocarbon has a value for the thermal conductivity approaching zero, the rate of heat transfer across the insulating jacket will be approximately directly proportional to the area touched by the hydrocarbon. On the other hand, if the value for the thermal conductivity of the same part of the inner wall of the container approaches infinity, the change in volume of the hydrocarbon will have no effect on the rate of heat transfer.

For most hydrocarbons, the decrease in volume on crystallization is about 5 to 10 percent. Assuming the most unfavorable case, where the rate of heat transfer will change directly with change in volume, and where the change in volume is 10 percent, the effect is to make the calculated amount of impurity too large by about 4 percent when $T_{z_0}-T_z$ is measured at one-fourth the total time of crystallization, and about 2½ percent when $T_{z_0}-T_z$ is measured at one-half the total time. Actually, the error from this source must be less than this because the thermal conductivity of the glass wall is several times that of the hydrocarbon in either the liquid or solid state. The error from this source may be reduced by placing within the freezing tube a close-fitting cylindrical tube of high thermal conductance of such length that it extends above the surface of the liquid substance but well below the level of the refrigerant.

The effect of the accumulation of solid substance on the walls of the container during crystallization, particularly after the cessation of stirring, is to decrease the over-all heat-transfer coefficient, and hence to lengthen the time of crystallization and make the estimated amount of impurity too large. However, as already mentioned, a decrease in the rate of crystallization of 10 percent from the initial to the final time of crystallization will have a much smaller percentage effect on the estimated amount of impurity. If the heat-transfer coefficient of the space between the substance and the jacket approaches that of the hydrocarbon in value, there will be a very significant change in the over-all rate of transfer of heat, and hence in the rate of crystallization, as the liquid hydrocarbon solidifies. If, however, the heat-transfer coefficient of the space between the substance and the jacket is very small in comparison with the heat-transfer coefficient of the hydrocarbon, there will be only a very small change in the over-all heat-transfer coefficient as the hydrocarbon solidifies and hence only a very small change in the rate of crystallization. The use of an insulating space having a very small heat-transfer coefficient, as provided by a silvered and well-evacuated vacuum flask, will reduce the error from this source. That is to say, a given rate of heat transfer between the substance and jacket should be obtained by using an insulating space with a low heat-transfer coefficient and an appropriate head of temperature.

Nonuniformity of temperature throughout the substance after cessation of stirring during the freezing experiment, from which time the temperature of that part of the substance around the thermometer is higher than that at the walls of the container, may influence the results in two ways. The correction for changing thermal head described in section II–3 is based on an ideal curve in which uniformity of temperature within the system is assumed. In the case of nonuniformity of temperature within the freezing tube, the rate of transfer of energy from the substance as a whole depends on the difference in temperature between the inner wall of the tube and the refrigerant rather than the difference in temperature between the thermometer and the refrigerant. In other words, the area above any actual curve, customarily used in correcting for change in thermal head, is not quite as large as the corresponding area above an ideal curve. Since the total correction for changing thermal head is large only in the case of small thermal heads and impure solutions, this part of the effect of

nonuniformity of temperature must be practically negligible in almost all cases. In the extrapolation (described in section II–3) which is made to take care of the fact that a portion of the energy transferred is used not in the crystallization, but in cooling the solid to the final temperature, the assumption of uniformity of temperature is made. If, as is actually the case, the temperature recorded is higher than the mean temperature of the solid, it is evident that additional energy has been transferred (and time elapsed) in cooling the solid below the recorded temperature. In other words, the value estimated for the total time is too long, which yields too large a value for the amount of impurity. To reduce the importance of this effect of nonuniformity of temperature, the stirrer may be made of a material of high thermal conductivity and designed so as to have sufficiently thick vanes traversing the substance. Keeping the thermal conductivity of the insulating jacket very small in comparison with the thermal conductivity of the substance also reduces the magnitude of the effect.

To take account of the fact that stirring energy is contributed to the substance only during the first part of the crystallization, a correction to the time of crystallization is described in section II–3. In making this correction, it is assumed that the energy of stirring is constant over the time the stirrer is in operation and equal to the value it has when the material is all in the liquid state. Since in the actual experiment, the stirrer is operated until one-fifth to one-third of the substance has crystallized, it is obvious that the presence of the solid material will increase the stirring resistance, and hence the rate of evolution of energy by stirring will be greater at the time of cessation of stirring than at the time crystallization is just beginning. The correction for stirring is, therefore, smaller than it should be. By using a stirrer that clears the inner wall of the container by several millimeters, and by stopping the stirrer as soon as a sufficient portion of the equilibrium freezing curve is obtained, the effect of change in the rate of evolution of energy by stirring may be minimized. In the experiments described in this paper, the stirring energy is about 2 percent of the total rate of transfer of heat between the substance and the jacket during freezing. In general, it is advisable to have the amount of stirring great enough to produce thorough mixing of the liquid and crystalline phases during the given period, but not so large as to be more than several percent of the total rate of transfer of heat.

Incomplete crystallization of the substance may occur in those cases where the impurity consists of one or more components having low freezing points, or where the impurity consists of a large number of components having freezing points below, or not far above, that of the major component, if the observations are not taken well below the temperature at which the last of these components of the impurity has crystallized out in the form of a eutectic with the major component. In such cases, when the amount of impurity is large and when the heat of fusion of the major component is small, a significant amount of the substance may remain uncrystallized even at temperatures 50° C or more below the normal freezing point of the major component. The total time of crystallization deduced from such observations will be too small, not only because some of the substance has not yet crystallized, but also because the slope of the "solid" line will indicate a rate of decrease of temperature not quite large enough. To reduce this error, which leads to too small a value for the amount of impurity,

it is necessary to use a large head of temperature between the substance and the jacket to permit observations to be taken to temperatures 75° C or more below the freezing point of the major component. For substances containing several mole percent of impurity, the foregoing is likely to be the source of greatest error.

The effect of a difference in heat of fusion between the impurity and the major component is to change the relation between the mole fraction of impurity in the liquid phase and the time of crystallization as given by eq 9. When the heat of fusion of the impurity is less than that of the major component, the observed time of crystallization is smaller than it would be with no difference in heat of fusion, and the effect is to make the estimated amount of impurity too small. When the heat of fusion of the impurity is larger than that of the major component, the effect is to make the estimated amount of im-

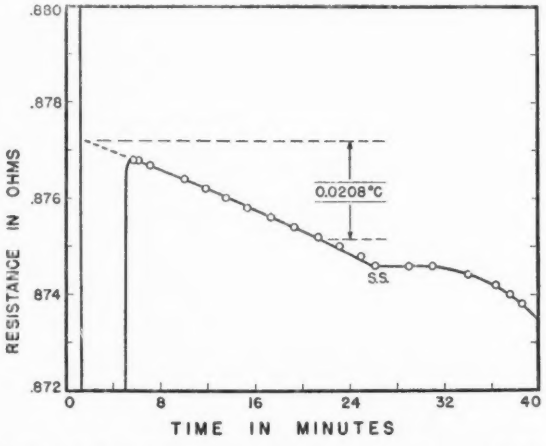

FIGURE 9.—*Part of a time-temperature freezing curve illustrating the sensitivity of the method.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer (0.1 ohm ≈ 1° C). The scale of abscissae gives the time in minutes. These observations were made on a lot of 1,2,3,4-tetramethylbenzene having an amount of impurity estimated to be 0.0006 ±0.0001 mole fraction. The circles are drawn with radii equal to 0.0005° C.

purity too large. When the amount of impurity is 0.01 mole fraction or less, the error from this source is usually negligible.

The effect of the inclusion of solute within the crystals of the major component is to raise the equilibrium portion of the freezing curve and consequently to yield too small a value for the amount of impurity.

The best criterion of the over-all effect of these uncertainties on the value of the amount of impurity estimated is that of making observations on known systems and comparing the estimates of impurity with the amounts actually present. The results of such comparisons are given in table 4, where the amounts of impurity estimated from time-temperature curves in the manner described on pages 599–602 in section II–3 are compared with the actual amounts known to be present in the given solutions. The six different solutions investigated were made from three main components and four different solutes, and the concentrations range from 0.0062 to 0.1147 mole fraction. Eight different results are listed because two independent time-tem-

perature curves were obtained on each of two systems. In seven of the experiments, the period of equilibrium extended far enough for the fraction crystallized to be taken as one-third, but, in one experiment, the period of equilibrium did not extend beyond the time when about one-fifth of the material was crystallized. From the results obtained, it appears that the amount of impurity can be estimated with an uncertainty not greater than about 10 percent of itself.

The sensitivity of this method and procedure for estimating the amount of impurity is illustrated by some observations made on 1,2,3,4-tetramethylbenzene isolated from petroleum [19]. In figure 9 is shown part of a complete freezing curve obtained with this substance. From the indicated lowering of temperature, which was measured from the initial time to the time when one-third of the material had crystallized, the amount of impurity in the original substance was calculated to be 0.00058 ±0.00006 mole fraction, or conservatively, 0.0006 ±0.0001 mole fraction.

TABLE 4.—*Summary of the estimates of the amount of impurity (solute) made on systems containing known amounts of impurity (solute)*

Solution			Estimation of the amount of impurity					
			Taking $r=1/3$			Taking $r=1/5$		
Main component	Solute added	Concentration of total solute [a]	$T_{2_0}-T_2$	Estimated amount of solute	Percentage error of the estimate	$T_{2_0}-T_2$	Estimated amount of solute	Percentage error of the estimate
		Mole fraction	° *C*	*Mole fraction*	*% of known amount*	° *C*	*Mole fraction*	*% of known amount*
2,2,4-Trimethylpentane.		(0.0018)	0.023	0.0018				
Do	*n*-Heptane	.0113	.140	.0111	−1.8			
Do	do	.0113	.147	.0117	+3.5			
Do	Methylcyclohexane	.0266	.368	.0286	+7.0	0.174	0.0272	+2.3
Do	do	.0266	.334	.0261	−1.9	.171	.0268	+0.8
Do	do	.0727	.977	.0726	−0.1	.480	.0718	−1.2
Do	do	.1147	1.373	.0985	−14.1	.695	.1010	−12.0
n-Dodecane		(.0012)				.005	.0012	
Do	1,2,4-Trimethylcyclohexane.	.0062				.027	.0068	+9.7
Toluene		(.0005)	.010	.0005				
Do	*m*-Xylene	.0126	.246	.0121	−4.0			
Mean value of the percentage error					[b] −(1.6 ±5.0)			[b] −(0.1 ±7.0)

[a] Values in parentheses refer to the original samples which were used to prepare the various solutions. The impurity was taken as equal to that estimated from the time-temperature cooling curves.
[b] The uncertainty assigned here is twice the standard deviation. See [17].

IV. CONCLUSION

The following points should be noted in connection with the procedure and discussion presented in this paper:

1. The procedure described for determining the freezing point and estimating the amount of impurity may be used only when the given substance crystallizes in such a way as to produce a freezing curve, a melting curve, or both, of which, in each case, a known portion represents thermodynamic equilibrium between the liquid and

crystalline phases. In this connection, the possibility must not be overlooked of the existence of a metastable equilibrium between the undercooled liquid and a crystal phase different from that which exists at the normal freezing point. See, for example, [9, p. 466].

2. While the lowering of the freezing point measures only the liquid-soluble, solid-insoluble impurity, this will represent substantially all of the impurity for the hydrocarbons obtained from petroleum, because the cases in which solid solutions occur in such systems are relatively rare. (See, for example, the work of Smittenberg, Hoog, and Henkes [15], who investigated a number of binary systems of such hydrocarbons and reviewed the earlier work in this field.) Further, any rational method of purification will leave in a given hydrocarbon only impurities that are very much like it in properties, and that, hence, will tend to form an ideal solution with it. For example, in the hydrocarbons separated from petroleum, the impurities most likely to remain in a given compound after purification will be aromatic impurities in an aromatic hydrocarbon, naphthenic impurities in a naphthene hydrocarbon, paraffinic impurities in a paraffin hydrocarbon. Less likely will be naphthenic impurities in a paraffin hydrocarbon and paraffinic impurities in a naphthene hydrocarbon, and least likely will be aromatic impurities in a paraffin or naphthene hydrocarbon and paraffinic or naphthenic impurities in an aromatic hydrocarbon.

3. From the data presented in table 4, it appears that estimates of the amount of impurity, determined by the procedure discussed in this paper, will be uncertain by not more than about 10 percent of the amount of impurity, for concentrations from about 0.005 to 0.1 mole fraction. For substances containing more than about 0.1 mole fraction of impurity, the uncertainty will very likely be greater, but, on the other hand, the need for the higher certainty on such very impure substances is correspondingly less. For substances containing less than about 0.005 mole fraction of impurity, the uncertainty of the estimates of impurity may be influenced largely by the precision of the measurement of temperature. For example, where the cryoscopic constant A is equal to 1/30 and r is equal to 1/4, values of $T_{z_0}-T_z$ equal to 0.01°, 0.001°, and 0.0001° C correspond to values of N_2^* equal to 0.001, 0.0001, and 0.00001 mole fraction, respectively. With hydrocarbons containing small amounts of impurity (about 0.001 mole fraction or less), it is usually necessary to have a thermometric sensitivity at least as small as 0.001° C, and to plot the appropriate part of the freezing curve on an expanded scale of temperature, in order to identify the portion of the curve representing thermodynamic equilibrium and to determine the lowering for a given fraction crystallized. For such compounds, departure from thermodynamic equilibrium during freezing frequently begins even before cessation of stirring.

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